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**RELATIVE PERMEABILITY AND WETTABILITY IMPLICATIONS OF
DILUTE SURFACTANTS AT RESERVOIR CONDITIONS**

A Thesis

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
In partial fulfillment of the
Requirements for the degree of
Master of Science in Petroleum Engineering
In
The Craft and Hawkins Department of Petroleum Engineering

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December 2005

DEDICATION

This work is dedicated to my parents, my wife Jill, and my siblings...

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My profound appreciation goes to God almighty, my maker who has helped me tremendously in all my academic endeavors. I will also like to appreciate, very profoundly, my major advisor Dr. Dandina N. Rao for his relentless help and guidance throughout the entire research experiments conducted for this thesis. The research afforded me the opportunity of gaining further insight into petroleum production technology, especially enhanced oil recovery processes. I am also very thankful to Dr. Anuj Gupta and Dr. Julius Langlinais of the Craft and Hawkins Department of Petroleum Engineering for their invaluable help and suggestions and for serving on the examining committee.

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NOMENCLATURE

N_{ca} = Capillary Number

v = Velocity, cm/sec

μ = Viscosity, cp

σ = Interfacial tension, Dynes/cm²

θ = Contact angle

\emptyset = Porosity, %

A = Area, cm²

L = Length, cm

Q = Flowrate, cc/hr

P_c = Capillary pressure

P_{nw} = Non-wetting phase pressure

P_w = Wetting phase pressure

R_1 and R_2 = Principal radii of curvature of the interface between the two fluids in the capillary tube

L_c = Characteristic length of core

K = Absolute permeability

K_e = Effective permeability

δ_w = Displacement by water ratio

δ_o = Displacement by oil ratio

V_{osp} = Volume of oil spontaneous displaced by water (cc)

V_{wsp} = Volume of water spontaneously displaced by oil (cc)

V_{wT} = Total volume of water spontaneously displaced by oil and forced (corefloods) displacement of water

V_{oT} = Total volume of oil spontaneously displaced by water and forced (corefloods) displacement of oil

I_w = Amott Wettability index

W = USBM wettability index

S_{wi} = Initial water saturation

S_{or} = Residual oil saturation

K_{ro} = End point relative permeability to oil at S_{wi}

K_{rw} = End point relative permeability to water at S_{or}

e_o and e_w = Corey exponents

h = Thickness

B_o = Oil formation volume factor

ABSTRACT

The improvement or increase of oil recoverable from discovered reservoirs has always been a very important issue as this helps to meet ever growing energy demand. Several methods have been put forward as means of achieving this objective. Chemical flooding, using surfactants has been considered in enhanced oil recovery processes. Surfactants are used primarily to lower oil-water interfacial tension (IFT) and thus improve production. However, surfactants possess the ability to alter rock wettability and hence increase oil production.

Previous investigations were performed at ambient conditions using stock tank oil. Extrapolation of the findings from the ambient conditions testing to reservoir conditions may be erroneous. Thus, reservoir condition investigations have been carried out using Yates live crude oils and Yates synthetic brine. Several coreflood experiments have been conducted at live reservoir conditions using two types of surfactants (anionic and nonionic) in varying concentrations. A core flood simulator based on JBN technique has been used to calculate oil-water relative permeabilities by history matching recovery and pressure drop measured during the corefloods. The simulated relative permeabilities have been used to infer wettability alteration based on Craig's rule of thumb to characterize wettability. The contact angle measurements, from previous investigations conducted at LSU, have been used to compare wettability alterations inferred from relative permeabilities. Furthermore, this study includes imbibition experiments as another means to infer wettability alterations by surfactants.

Native wettability has been established for the Yates field using the Amott's wettability index and changes in the wettability indices with varying surfactant concentration have also been measured. These changes have been interpreted to infer

wettability alteration. The use of nonionic ethoxy alcohol surfactant at different concentrations with Yates live crude oil in corefloods experiments showed significantly higher oil recoveries indicating that the surfactant has altered wettability. The optimum surfactant concentration has been established at 1500 ppm. Other experiments conducted using the anionic ethoxy sulphate surfactant have not shown a favorable wettability alteration as Yates core was altered from weakly water-wet to weakly oil wet consequently lowering oil recoveries.

Oil-water emulsions have been observed at higher concentrations of both surfactants. The emulsions caused high pressure drop during the wettability alteration investigations and thus affected the interpretation of Craig's rules-of-thumb in inferring wettability alteration. The oil recovery plots show a step wise increment in recoveries due to flashing of live oil in the production string and emulsion formation and resulting blockage and release in the flowlines.

The imbibition tests and coreflow experiments conducted in this study have provided an insight into effect of surfactants on wettability alteration at both ambient and reservoir conditions using stocktank oil and live reservoir fluids and the improvement in oil recoveries as a result of wettability alteration. Analysis of results with capillary pressure number showed the importance of contact angle in capillary number estimation.

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Today's energy needs are met in large part by crude oil. The U.S Department of Energy estimates that nearly 377 Billion barrels of discovered oil are left behind after conventional primary and secondary production techniques have been employed (USDOE). These huge amounts of oil left are deemed "unrecoverable" by present technologies. Several methods have been put forward to increase or enhance the recovery from these reservoirs and hence reduce the amount of oil left behind. One of these methods is wettability alteration.

Alteration of wettability of porous rock material has been shown to be possible by several previous investigations (Spinler et al, 2002, Ayirala, 2002, Ayirala and Rao, 2004). The success of wettability alteration is seen as the increment in percentage of recoverable oil, depending on natural wettability. Several methods have also been applied to enhance the recovery of oil by reducing oil viscosity, interfacial tension and/or supplement the natural energy of the reservoir.

Literature review showed that usage of surfactants to improve oil recovery has been previously applied based on the mechanism of reduction in interfacial tension (IFT). However, a great deal, if not all of the investigations conducted were carried out at ambient conditions and using stock tank fluids. Ayirala (2002) carried out extensive investigation on wettability alteration using Yates reservoir rock and fluids in a reactive and non-reactive system. The positive findings of the investigation prompted further experiments of wettability alterations at reservoir conditions conducted in this study.

There currently exists a gradual but steady departure from carrying out oil reservoir investigations at reservoir conditions, to a preference for ambient conditions, due to ease in operation. The snag in this scenario is that the results obtained from investigations at ambient conditions and stock tank fluids, when extrapolated to reservoir conditions could lead to unrealistic, complex and unexplainable difficulties in field applications. The outcome is that the oil and gas industry is skeptical about implementing the results of such experimental investigations for field processes.

Therefore, in order to extend the laboratory result to field, the surfactant induced wettability alteration investigations for Yates field was carried out in the laboratory at Yates reservoir conditions of 82 °F and 680 psia, using Yates live oil. The live oil was made up by charging Yates stocktank oil with crude oil constituents, as analyzed by a commercial laboratory. The investigation is divided into two parts for meaningful interpretation of observations. The first part consists of coreflood experiments carried out at reservoir conditions using live oil and the second part involves imbibition tests of Yates field core to determine the Amott wettability index of the core and hence wettability. The Amott wettability tests were carried out at ambient conditions, as this condition is required for spontaneous imbibition tests.

The crude oils in the reservoir, possess great variation in chemical composition, which is directly related to the formation environment. The differences in these reservoirs complicate the understanding of mechanisms that aid flow of oil from the reservoir to the surface. The improved oil recovery processes are receiving more attention now than in the past. This is driven by the current high prices of crude oil and the ever increasing demand.

Petroleum reservoir is a geologic formation, with impervious layer or faults that trap oil and reservoir brine from further migration and hence form an accumulation of oil in the reservoir. These brines co-existing with the oil contain some surface-active components, which affect degree of solubility to the crude oil in brine affecting the wettability of the reservoir (Ma et al, 1996, Zhang et al, 2004) Wettability is to a large extent dependent on the mineralogy of the host rock surface and interactions that takes place between the crude oil, brine and rock surface (Schembre et al, 2004).

Two well-characterized surfactants namely ethoxy alcohol and ethoxy sulfate, were used for in this investigation. The concentration of these surfactants was varied from 0 ppm to 5000 ppm. Concentration of surfactant corresponding to optimum recovery was obtained and compared to previous results of investigations conducted at ambient conditions, using stocktank oil. The wettability and wettability alteration of the Yates field core sample was also inferred from imbibition investigations. All the results from these investigations were compared with the results of other investigations conducted on quantifying the effect of surfactant on wettability by measuring contact angle. It is expected that the results of this investigation will provide more realistic information on surfactant-induced wettability alteration process at reservoir conditions and hence enable decisions concerning field implementation of the process.

Reservoirs possess different wettability conditions. The extensive literature available in these fields of wettability shows that imbibition tests and contact angle measurements are two most commonly used methods in characterization of reservoir wettability. An attempt is made in this investigation to study the wettability alteration of Yates naturally fractured core at reservoir conditions. The findings are further compared to previous

coreflood results of investigations conducted using Yates stocktank oil and to the results of the imbibition tests carried out on the Yates core at ambient conditions.

CHAPTER 2

LITERATURE REVIEW

This experimental investigation is focused on characterizing the effect of dilute concentration surfactant on wettability alteration at reservoir conditions as well as surfactant effects on imbibition as it affects enhanced oil recovery. Therefore, up-to-date literatures on various aspects considered in this investigation are reviewed in-depth in this chapter with emphasis on imbibition and wettability alteration.

2.1 Background on Enhanced Oil Recovery

The need for enhanced oil recovery stems from diminishing inherent power of the reservoir with time to produce oil on its own. EOR is the alternative for revitalizing mature reservoirs. The target oil for EOR operations is the residual oil left behind after primary and secondary production modes. EOR is defined as the recovery of additional oil from the reservoir by the injection of material not normally present in the reservoir.

Oil production from a reservoir can be classified into primary, secondary and tertiary recovery modes. Primary recovery constitutes oil produced by inherent natural mechanisms present in the reservoir. Natural oil recovery mechanisms include solution gas, water influx and gas cap or gravity drainage (Muskat, 1949). Secondary recovery refers to techniques such as water injection and gas cap injection. The main purpose of this type of recovery is reservoir pressure maintenance. Tertiary recovery techniques on the other hand refer to any production technique applied after secondary recovery processes. These include chemical flooding, miscible processes and thermal processes.

Enhanced oil recovery processes provide supplementary mechanism to depleting natural mechanism of the reservoir such as pressure maintenance, oil mobility control and wettability alteration.

2.2 Wettability Definition

The wettability of a reservoir is defined as the actual process by which a liquid spreads on (wets) a solid substrate or surface. Wettability can be determined by measuring the contact angle. Wettability of porous medium is important in determining the displacement effectiveness of injected fluids and ultimate oil recovery. Kovscek et al. (1993) observed that wettability is a prime factor in controlling multiphase flow and phase trapping since wetting fluids occupy the smallest, tiniest and most hydrodynamically resistive pore channel. Homogenous wettability of pore media are broadly classified into three (4) categories namely (i) water-wet, (ii) oil-wet (iii) intermediate-wet and (iv) heterogenous state of wettability know as mixed-wet. Wetting characteristics of a reservoir is an important factor in determining residual oil saturation after a given production process. An oil-wet formation tends to hold back more oil in its minute pores and produce reservoir water. The alteration of reservoir wettability from oil-wet to water-wet or mixed wet may help in the production of more oil from such a reservoir.

2.3 Imbibition Definition

Oil recovery from naturally fractured reservoirs usually occurs by spontaneous imbibition process, which makes this an important phenomenon in oil production from reservoirs (Morrow and Mason, 2001). Imbibition can be defined as the process of absorbing a wetting phase into a porous rock or the capillary suction of a wetting phase into a porous

medium. It is also defined as the intake of a wetting phase into pore spaces of a porous media by capillary forces. The opposite of imbibition phenomena is the drainage process. Drainage is defined as the process of forcing a non-wetting phase into a porous rock, thereby resulting in a decrease in the wetting phase saturation. Oil migrates into most reservoirs as the non-wetting phase, decreasing the water saturation, therefore initial charging of the reservoir is a drainage process. Imbibition is very important for oil recovery from hydrocarbon reservoirs. It results from the effect of capillary pressure, which ultimately creates a surface energy with a tendency to absorb liquids that come into contact with such surfaces. The extent of this absorption or adsorption is thus an indication of the wettability of the porous medium (Buckley, 2001)

Imbibition and drainage can advance or hinder water movement depending on the wettability of the reservoir rock, which has a great impact on the ultimate oil recovery from the reservoir (Morrow and Mason, 2001., Morrow and Tang, 1999). Imbibition is interconnected with other natural phenomena such as wettability, contact angle, capillary pressure and hysteresis. Reservoir rocks may imbibe both water and oil at reservoir conditions. The phase that is preferentially imbibed in larger amounts in a multiphase fluid system is usually the wetting phase.

2.4 Imbibition Types

Imbibition can also be broadly categorized as spontaneous and forced, a narrower classification is co-current and countercurrent. Spontaneous imbibition is predominant in naturally fractured hydrocarbon reservoirs with low permeability. The imbibition of the reservoir rock by the wetting phase, i.e. water in a water-wet rock, is observed as production at the surface. Buckley (2001) defined forced imbibition to be the application

of pressure to the water phase to overcome capillary forces, hence production of oil is enhanced. Morrow and Mason (2001), defined forced imbibition to be the recovery of oil by forcing water through a porous medium under a pressure gradient, as demonstrated in laboratory core flood experiments. Co-current and counter-current are normal imbibition types. Co-current imbibition occurs when both the inlet and outlet are open to an invading fluid. Countercurrent imbibition occurs when only one of the ends (Inlet) is open. Both imbibition mechanisms are of unique importance in understanding reservoir imbibition phenomenon. Counter-current conditions are mainly used for imbibition measurements in the laboratory, while co-current imbibition has been suggested to be a major factor in recovery processes from naturally fractured reservoirs. Co-current imbibition is characterized by a higher and faster recovery, due to gravity segregation of oil and water in the fractures. Zhang et al (1986) also carried out studies to improve scaling of spontaneous imbibition by using twenty Berea sandstone cores with length ranging from 1.17 to 10.24 cm and boundary conditions of AFO (al- face-open), TEO, OEO (one-end-open), and (TEC) two-ends-closed. Oil viscosity was ranged from 1 to 156 cP in Zhang et al investigations. Mattax and KYTE (1962) also investigated imbibition scaling using alundum and sandstone media, with length ranging from 1.1 to 4.35 inches and boundary conditions of AFO and OEO. Figure 1 is a plot of capillary pressure against water saturation. It shows areas of forced and spontaneous imbibition. The oil is displaced by imbibition of water into the minute pores in the positive capillary pressure region. Recovery of oil by the drainage process is accomplished by water invasion of the larger pores, this is more common in oil-wet rocks.

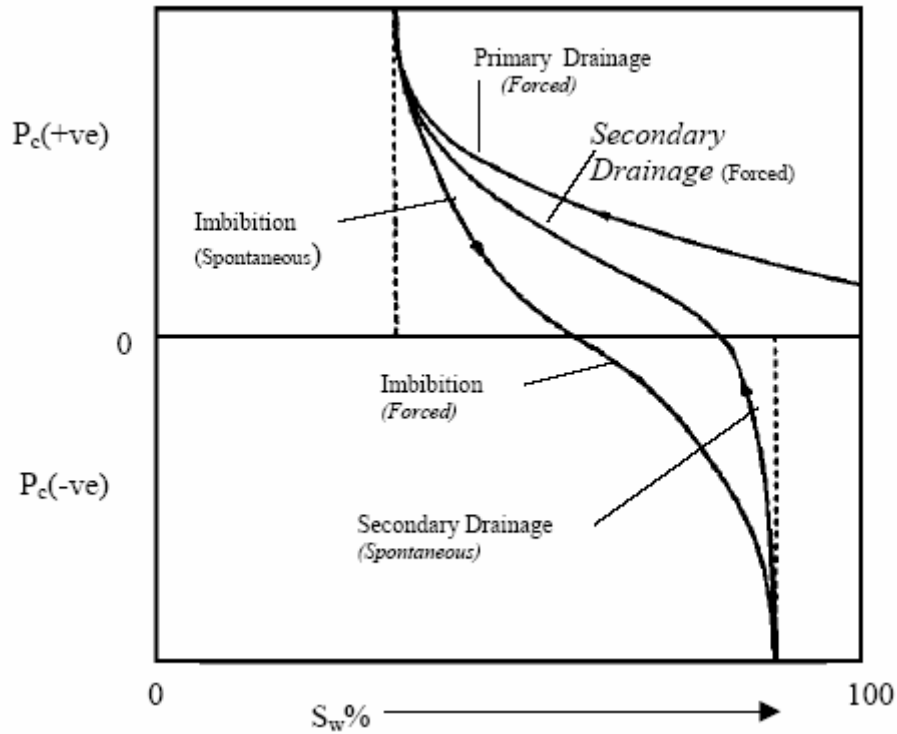


Figure 1: Diagrammatic Representation of Forced and Spontaneous Imbibition. (Morrow and Mason 2001)

Morrow and Mason (2001) reported that continuous production of crude from oil reservoirs after the initial prolific oil production is due to the imbibition of reservoir brine into the rock pore spaces. Tremendous amounts of crude oil have been recovered by spontaneous imbibition from the North Sea Chalk and Ekofisk reservoirs. Imbibition has been widely researched for the last 50 years, with investigations still being conducted to further understand this process in its entirety. Imbibition process is a natural process happening in several fractured reservoirs.

2.5 Fundamentals of Imbibition

Imbibition has been previously described as an after effect of capillary action in porous media (Zhou et al., 1996). There is interdependency between capillary pressure, fluid saturation and media wettability. The study of wettability in porous media and fluid

constituents of the pores has been an exciting and important aspect of improved oil recovery research. It has been observed that capillary pressure wields a strong influence on imbibition as shown earlier in Figure 1. Capillary pressure can be defined in reservoir terms to be the difference in interfacial pressure between two immiscible fluids. This interface, which usually is at equilibrium, is dependent on the preferential wetting of the porous media. Capillary pressure is defined as the difference in pressure between the interface of a wetting and non-wetting phases Donaldson and Djebbar (1996);

$$P_c = P_{nw} - P_w \quad (1)$$

Where P_c , is capillary pressure, P_{nw} is pressure in the non-wetting phase and P_w is the pressure in wetting phase fluid. A wetting fluid is the fluid that is preferentially adsorbed on the rock surface and minute pores of rocks.

When two fluids wet the walls of a medium to the same extent, the interface created is straight, the contact angle is 90° and the capillary pressure across such surface is zero. If water and oil are in a porous media, e.g. a capillary tube, the interface of the two immiscible fluids will be curved in either the direction of the oil or water. A curvature of interface directed towards oil, indicates a higher pressure in the water and hence a negative capillary pressure in a water-wet tube or vice versa. The radius of curvature at the interface of oil and water in reservoir rocks is dependent on various factors such as; wettability, fluid saturations, pore walls mineralogy, pore geometry and the saturation history of the system, which is dynamic with progress in oil production from the reservoir. Collectively, these factors cause the radii of curvature and contact angle of the fluids to vary from pore to pore within the media, Donaldson and Djebbar (1996). From a macroscopic observation, the wettability of a medium is dependent on the

contact angle that the oil-water interface makes with the surface of the solid medium, such as in an oil/water system. Anderson (1986), Donaldson and Djebbar (1996) studied contact angle existing for water and oil in contact in a capillary. They showed that contact angles of $0^\circ < \theta < 70^\circ$, $70^\circ < \theta < 110^\circ$ and $110^\circ < \theta < 180^\circ$ are indicative of a water-wet, neutrally-wet and oil-wet systems respectively. The importance of contact angle in imbibition phenomenon stems from its direct relationship with wettability. Contact angle is the angle between the liquid-liquid interface and the surface medium, and is usually measured through the denser phase. It indicates the relative wetting tendencies of the fluids in contact with the solid medium.

Washburn (1951) investigated co-current imbibition in a capillary tube to show interactions between capillary driving forces and viscous resistance. The results of the investigation analyzed for spontaneous displacement of air by mercury were used to develop capillary pressure correlations. He postulated that if a capillary tube of radius, R , contains a perfectly wetting liquid (Cosine $\theta=1$ or $\theta=0$) with surface tension σ , the capillary pressure P_c , is given by:

$$P_c = \sigma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad (2)$$

Where, R_1 and R_2 are the principal radii of curvature of the interface between the two fluids in the capillary tube. For equal principal radii of curvature in the capillary tube, equation (2) becomes

$$P_c = \frac{2\sigma}{R} \quad (3a)$$

Equation 3a is known as the plateau equation (Donaldson and Djebbar, 1996). For a non-perfectly wetting fluid, a contact angle exists between a droplet of the fluid and the media

surface with which a contact is made. Therefore cosine θ is not equal to zero (Cosine $\theta \neq 0$) in such cases. All known reservoir fluids are not perfectly wetting fluids. Equation (3a) modified for the contact angle phenomena becomes equation (3b)

$$P_c = \frac{2\sigma \cos \theta}{R} \quad (3b)$$

where θ is the contact angle and other terms have been previously defined. These equations are modified for dimensionless time in imbibition scaling as discussed below.

2.6 Laboratory Imbibition Scaling

The results of imbibition tests carried out in the laboratory are often scaled to reservoir conditions. A scaling group was defined by Mattax and KYTE (1962) as the ratio of capillary force to viscous resistance. The complexity of an actual reservoir cannot be duplicated in the laboratory, for this reason some inherent errors are observed in the scaling models developed. One of the positive attributes of scaling is the identification of very important reservoir characteristics and conditions which greatly affect imbibition. Adequate analysis of these factors helps predict and improve oil recovery.

Several factors are considered in the scaling of imbibition. These factors include liquid/rock interaction, fluid viscosity, rock properties, interfacial tension, wettability and core geometry. Several scaling methods have been developed for reservoir with different wetting characteristics, but most were based on oil production from very strongly water wet reservoir rocks (VSWW).

Morrow and Mason (2001) developed a relationship for imbibition scaling from Washburn's analysis of imbibition into capillary tube using the poiseuille equation.

$$\frac{\Delta P}{L} = 8 \frac{\mu v}{r^2} \quad (4)$$

Where L and r are the tube length and radius respectively, these are related to the viscosity μ , velocity V , and a pressure drop ΔP of fluid in the tube.

A fluid of viscosity μ , which is displacing another fluid of negligible viscosity in a capillary tube, has a driving pressure P_c and a viscous resistance, which is proportional to the length of tube invaded. This relationship was shown by Morrow and Mason (2001) from the combination of equations (3i) and (4).

$$v = \frac{2\sigma}{r} \frac{1}{L} \frac{r^2}{8\mu} = \frac{\sigma r}{4\mu L} \quad (5)$$

The drawback in equation (5) is the perfectly wetting fluid assumption made in equation (3i). Substituting dL/dt for velocity and integrating equation 5;

$$\int_0^L L dl = \int_0^t \frac{\sigma r}{4\mu} dt \quad (6)$$

$$L^2 = \frac{\sigma r t}{2\mu} \quad (7)$$

Equation 7 is the basis from which the derivation of the relationship for imbibition into a tube can be scaled using the dimensionless time defined by

$$t_d = \frac{\sigma r t}{f(\mu_w, \mu_o) L_{\max}^2} \quad (8)$$

Where t_d is dimensionless time and σ is interfacial tension (IFT) and μ_w, μ_o are viscosities of water and oil respectively. L_{\max} is also known as the characteristic length L_c of the test core sample. Establishing a representative viscosity for water and oil in contact is rather difficult, the function $f(\mu_w, \mu_o)$ is representative of the geometric mean of the viscosities of water and oil respectively.

The microscopic radius, r , is proportional to the square root of ratio of permeability, K , and porosity, ϕ (Zhou et al. ⁸). Substituting this into equation (8) yields equation (9), which is usable form of the dimensionless time equation for imbibition scaling.

$$t_d = t \sqrt{\frac{K}{\phi}} \frac{\sigma}{\sqrt{\mu_w \mu_o}} \frac{1}{L_c^2} \quad (9)$$

Equation (9) shows that dimensionless imbibition time is a function of viscosity of fluids in the media, characteristic length of the media being investigated, interfacial tension between the fluids and time. The dimensionless scaling factor shows the differences in imbibition of fluid into a limited number of types of strongly water-wet media. The constraint in the applicability of equation (9) to all media is due to inclusion of $\sqrt{k/\phi}$. This is because the value of permeability and porosity differs from one medium to another, also, permeability may not be uniform throughout an entire medium. More investigations involving this type of correlation are required for the applicability of the dimensionless time equation to a wider variety of rocks (Tang and Morrow 1999).

Figure 2 is a comparison of plots of normalized oil recovery with dimensionless time for very strongly water-wet (VSWW) reservoir. It shows recoveries from laboratory tests conducted by several independent investigators. The plots were developed by Mattax and Kyte, (1962); Hammon and Vidal, (1986), and Zhang et al., (1996). It showed a consistent trend in the data by the three independent investigations. They observed that the trend in oil recovery was similar for all very strongly water wet cores (VSWW) that were used to carry out the investigation with dimensionless time. This observation also showed the importance of core characteristic length.

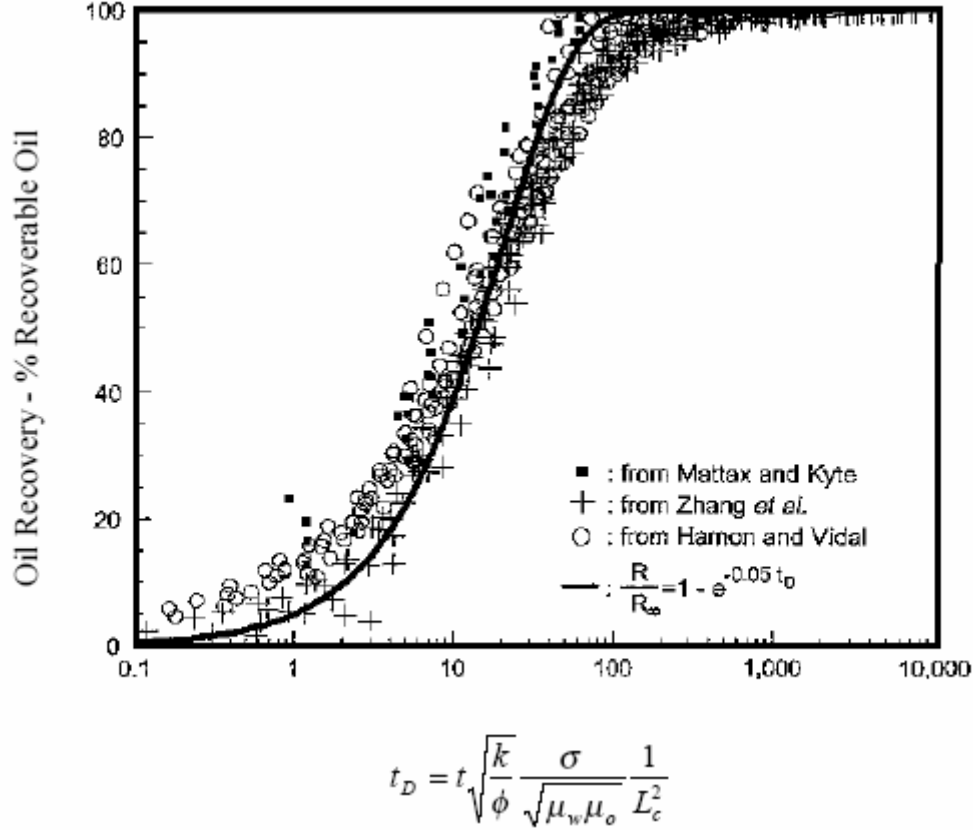


Figure 2. Plot of Normalized Oil Recoveries versus Dimensionless Time for Very Strongly Water Wet (VSWW) Cores. (Ma et al, 1995)

Another important factor in imbibition scaling is the characteristic length L_c of the core sample. It is determined by the size, shape and boundary conditions of a sample.

Zhou et al., (2001) defined characteristic length L_c from Mattax and Kyte (1962) investigation as:

$$L_c = \sqrt{\frac{V}{\sum_{i=1}^n \frac{A_i}{X_{Ai}}}} \quad (10)$$

Where V is the bulk volume of the core sample, A_i the imbibition face area, and X_{Ai} is the distance traveled by imbibition front from open surface, A_i , to the no-flow boundary. Dimensionless time t_d , is a function of this characteristic length L_c as shown in

equation (9). Hammon and Vidal (1986) investigated factors that affect characteristic length, L_c , using aluminum silicate cores with lengths varying from 10 to 85 cm and different boundary conditions (core surface open or closed to imbibition) ; all-face-open (AFO), two-ends-open (TEO) and one-end-open (OEO). They used same oil and water phase in their investigations. Zhang et al (1986) also carried out studies to improve scaling of spontaneous imbibition by using twenty Berea sandstone cores with length ranging from 1.17 to 10.24 cm and boundary conditions of AFO, TEO, OEO, and (TEC) two-ends-closed. Oil viscosity was ranged from 1 to 156 cP in Zhang et al investigations. Mattax and Kyte (1962) also investigated imbibition scaling using alundum and sandstone media, with length ranging from 1.1 to 4.35 inches and boundary conditions of AFO and OEO. Figure 2 shows that data on oil recovery from strongly water-wet media can be correlated fairly accurately using equation (9) and an oil recovery function defined for a strongly water wet system as:

$$\frac{R}{R_{\infty}} = 1 - e^{-\alpha t_d} \quad (11)$$

Where R is oil recovery by imbibition, R_{∞} is ultimate oil recovery by imbibition and α is the oil production decline constant. The average value of α is 0.05 for the curve shown in Figure 2, Hognesen et al. (2004) in their investigation of scaling laboratory results to field, observed that all parameters scale quite agreeably, except when the shape factor of the cores was used as the characteristic length. However, a substitution of height and diameter for the core at low value of interfacial tension (IFT) did not scale quite well, but the usage of only the height of core as the shape factor showed a good fit in plotting of the normalized oil recovery against dimensionless time, t_d . The fit of the scaling

obtained with the use of the height of core as shape factor indicates the effect of gravity forces in oil recovery mechanism. Li and Horne (2000) observed that scaling by dimensionless time conducted in a study could explain the lower imbibition rates in systems with high IFT than in systems with low IFT.

2.7 Wettability Measurement Techniques

Imbibition tests are used for the comparison of the imbibition tendencies of water and or oil into a rock in a two fluid system. Water may imbibe into hydrocarbon reservoir rock interstices at low saturations displacing excess oil from the surface of the rock grains in a water-wet rock condition, or oil may imbibe at low insitu oil saturations displacing excess water in an oil-wet condition. Imbibition/wettability tests, such as the Amott method, Amott-Harvey which is a modified version of the Amott method, and USBM test can be used to determine hydrocarbon rock wettability.

2.7.1 Amott Method

The Amott test is a well-known test for the determination of the wettability of reservoir rock and it is based on the principle of spontaneous and forced imbibition of oil and water into the cores (Amott, 1959). The main principle of this method is that the wetting fluids spontaneously imbibe into the core displacing the non-wetting fluid. A centrifuge is used to further force the wetting fluid to imbibe more into the rock pore space, and hence forcefully displace the non-wetting fluid. The difference in ratio of the volume of fluid spontaneously imbibed to the total (spontaneous and forced) fluid imbibed is used to determine the index. This test is usually carried out in five stages (Anderson, 1986) , (Donaldson and Djebbar,1996):

- i. Core at irreducible water saturation (S_{iw}) is brought to residual oil saturation (S_{or}) by flooding brine for sufficient time to forcefully displace oil from the pores. Coreflood was carried out by using Hassler type coreholder.
- ii. The core is immersed in oil in an imbibition cell for sufficient time (14 days) to allow for spontaneous imbibition of the oil and displacement of brine in the pore spaces and the volume of displaced brine is recorded as V_{wsp} .
- iii. The water is further displaced by coreflooding at 90cc/hr to irreducible water saturation (S_{iw}), the total amount of water displaced by spontaneous and forced displacement is recorded as V_{wT} .
- iv. The core is immersed in brine for sufficient time for 14 days in this experiment, and the volume of oil displaced spontaneously is measured and recorded as V_{osp} .
- v. The oil in the core is then forcibly displaced by water to S_{or} in the centrifuge and the total amount of oil displaced by imbibition and forced displacement is recorded as V_{oT} .

The Amott wettability index is expressed as a relative wettability index, that is the difference between the displacement by oil ratio and displacement by water ratio;

$$I_w = \frac{V_{osp}}{V_{ot}} - \frac{V_{wsp}}{V_{wt}} = (\delta_w - \delta_o) \quad (12)$$

The water-wet cores are usually characterized by a positive displacement by water ratio, δ_w , and a low value (near zero) for displacement by oil ratio, δ_o . A zero value of I_w is usually observed for the neutrally-wet cores, which indicates the absence of spontaneous imbibition of both oil and brine or equal amounts of both fluids imbibing

spontaneously. A value approaching unity for the displacement by water ratio δ_w , shows a very strongly water wet sample (VSWW), while a weakly water wet sample is usually characterized by a lower value of about 0.30. Neutrally-wet cores are characterized by a value near zero for both ratios. The Amott technique shows an important relationship between rock wettability and imbibition. Amott test is interpreted for wettability measurement to vary from +1 for complete water wetness to -1 for complete oil wetness. Cuiec (1984) further narrowed down the interpretation of the wettability index by stating that the system is water-wet when $+0.3 \leq I_w \leq 1.0$, intermediate (or neutral) wet when $-0.3 \leq I_w \leq 0.3$ and oil wet when $-1 \leq I_w \leq -0.3$. The disadvantages of this method are its insensitivity at neutral wettability states and the inability to be adopted to reservoir conditions of pressure and temperature.

2.7.2 Amott-Harvey Method

This is a modified Amott method of imbibition measurement. It is carried out with the addition of one more step to the core preparation before commencement of the test. The core is initially centrifuged under brine and then under crude oil to reduce core to initial water saturation. This is followed by the steps enumerated in the Amott method for the wettability determination. Amott-Harvey relative displacement index is the displacement by water ratio minus the displacement by oil ratio.

2.7.3 USBM Wettability Test

This test was developed by Donaldson (1969). It is mostly used for measuring wettability than for measuring imbibition. It does not depend on spontaneous imbibition. However, it works on the principle of a non-wetting phase requiring more energy to displace a wetting phase and vice versa. Therefore the ratio of the area under the capillary pressure

curves between irreducible water saturation and residual oil saturation is a direct indicator of wettability. This is therefore a special measurement of forced imbibition using a centrifuge.

Other methods of inferring wettability include the contact angle method. This is an accurate method used when pure fluids and artificial cores are used. This method of wettability inference carried out using the sessile drop technique, modified form of sessile drop technique, wilhelmy plate technique and the Dual-Drop Dual Crystal (DDDC) technique. The relative permeability method may also be used to infer wettability.

2.8 Imbibition and Rock Mineralogy

Oil production from fractured reservoirs with favorable wettability normally occurs by spontaneous water imbibition, which helps to expel oil from matrix into fracture network. This reason makes spontaneous imbibition a very important factor to be considered in oil recovery processes from fractured hydrocarbon reservoirs (Rao and Ayirala, 2000). Several investigators have shown that some chemical interactions exist between reservoir rock surfaces and the oil and brine contained in the rock pores. However, the extent and implications of the complexities arising from these interactions have not been characterized for various reservoir types.

Tang and Morrow (1999) investigated crude oil/brine/rock interactions and showed that an increase in recovery of crude oil with decrease in salinity was obtainable from numerous laboratory experiments carried out on a single reservoir sandstone core. The Berea sandstone cores, used in the experiment were aged and stabilized by firing

them at 800°C. It was thus established that crude oil presence was a necessary condition for sensitivity to salinity of the brine.

Egermann et al. (2004) carried out extensive numerical studies of water-gas imbibition in vuggy carbonates. The results of these studies which corroborated previous laboratory findings showed that spontaneous water imbibition was low in tight and vuggy carbonates. This was perceived to be caused by the core's low relative permeability to water. Other reasons ascribed to this observation in the rock cores, were the uniqueness of porous structure with fairly large vugs dispersed within a tight matrix with very small pore throats, which tends to have an effect on capillary pressure that does not enhance spontaneous imbibition (Li et al., 2003).

Akin and Kovscek (1999) observed certain interesting results in their study of high porosity, low permeability diatomites of California. Capillary forces dominate multiphase flow in diatomites, but the prediction and understanding of these capillary forces are still evolving due to limited capillary pressure data on diatomite. Imbibition tests conducted on diatomite cores showed some vague similarities to those of Berea sandstones which was used for comparison. The experiments were limited to spontaneous co-current imbibition on diatomite, monitored by a CT scanner. It was observed that oil imbibition fronts in absence of initial water saturation are sharp during the spontaneous oil imbibition process. This suggests that all pore sizes fill simultaneously which implies a good pore structure interconnectivity of the diatomite rocks. However, this pore communication is not reflected in oil recovery from diatomite reservoirs, which has been characterized with low recoverable factor of the oil in place, example is the Californian fields.

Schembre et al., (2004) studied temperature effect on diatomite wettability. It was observed that increased temperatures reduced the oil-to-water viscosity ratio. This caused a less resistant force to water imbibition, and further improved water-wetness of the media, hence the imbibition rates and extent of oil recovery by spontaneous imbibition. The effect of temperature on residual oil saturation was marginal. Further interpretation of experimental results shows that a mechanism for wettability shift towards increased water-wetness at high temperatures exists in diatomites, as fines detach from oil coated pore walls, which exposes the clean water-wet rock surface underneath.

Standnes and Austad (2002) studied temperature effects in carbonate reservoirs and observed an increase in oil-wetness as temperature decreases. They suggested an alteration of wettability of the oil-wet carbonate reservoir cores using surface active agents for further investigations. This is expected to improve spontaneous imbibition into the matrix blocks and hence increase oil recovery. Standnes and Austad (1999), further observed that wettability induced by crude oil on chalk surfaces, is dependent on the amount of acidic components in the oil, hence crude oils with high acid number have a greater potential of turning chalk oil-wet, this is however independent of the amount of asphaltene in the crude oil.

2.8.1 Imbibition Wettability and Wettability Alteration

The interdependence of imbibition and rock wettability evaluation has made separation of the two terms rather impossible. Spontaneous and forced imbibition can be correlated reasonably with other wettability indicators (Glothin et al., 1990). Wettability of a reservoir rock is one of the important factors to be considered in the development plans of a new field. Until the early 80's, it was assumed that almost all reservoirs were water-

wet (Cuiec 1984). However, more recent studies have proven this to be an erroneous assumption (Standnes and Austad 1999). Most oil-wet reservoirs have recoveries that are less than those from water-wet reservoirs having the same OOIP. This is explainable partly from imbibition phenomenon and other complex interactions occurring in the reservoir during production (Akin and Kovescsek 1999).

Many naturally fractured hydrocarbon reservoirs continue to produce mainly by spontaneous imbibition after the primary production from inherent energy is complete. Zhou et al., (1996) showed in a detailed form, the sensitivity of spontaneous imbibition to rock wettability. They reported that oil recovery by spontaneous imbibition passes through a maximum in recovery with change in wettability from very strongly water-wet (VSWW) to moderately water-wet conditions. They however did not categorize recovery from oil-wet reservoirs. Wettability alteration of solid surfaces cause changes in the distribution of fluids in the porous medium, and this has a profound effect on capillary pressure and relative permeabilities of fluids. It also affects fluid flow characteristics and hence ultimate recovery of the non-wetting phase from the reservoir by imbibition.

The alteration of reservoir wettability from oil-wet to water-wet therefore becomes of paramount importance in order to enhance the recovery from oil-wet reservoirs. Several different viewpoints have been expressed on wettability alteration. Some literature reviewed favored surfactants, while others found that temperature increments (thermal method) will work better in altering wettability and that it is less expensive compared to the chemical methods. These studies are briefly discussed below.

Fleury et al., (1999) studied the effect of wettability on oil recovery, using chemical additives that change the surface properties of natural samples while keeping

interfacial tension and viscosity constant. The results obtained from their experiments using sandstone samples treated with water soluble potassium methyl silicate, showed that final oil saturation (S_{or}) was reduced from 0.4 to 0.3 and 0.1, with a minor modification on the primary drainage capillary pressure curve, depending on how the treatment system was conducted. Wettability is known to have a strong impact on water flooding processes with high chances of better recovery rates being observed in intermediate or mixed wetting conditions as reported by Jadhunandan and Morrow (1995)

The optimum recovery of hydrocarbon material from oil bearing reservoirs has been established to be associated with the wetting of the reservoir rock by both water and oil (hydrocarbon and brine), usually referred to as mixed wettability. The wetting phase in a rock imbibes more easily than the non-wetting phase which creates a very strong interaction between wettability and imbibition as has been shown in many studies.

2.8.2 Effects of Surfactants on Imbibition

Surfactants can be used to alter rock wettability from oil-wet to water-wet hence increase spontaneous water imbibition and improve recovery (Morrow and Mason, 2001). Surfactants are defined as surface active agents. They lower surface tension between two or more incompatible phases. Soaps, detergents, wetting agents, solubilizing agents, and emulsifying agents are typical surfactants. They are further classified as anionic, cationic, nonionic and amphoteric. These classifications are based on their charges. The anionic surfactant is negatively charged, the cationic surfactant is positively charged and thenon ionic surfactants have no electric charge at all. Surface-active compounds with both acidic and alkaline properties are known as amphoteric surfactants. The key functional

groups in the chemical structures of the surfactants are the nitrogen and the carboxylic groups (Priyanto et al., 2001).

A broader classification of surfactants is based on their nature such as hydrophilic and hydrophobic surfactants. The chemistry of surfactants is rather complex due to variations in their chemical characteristics and their diverse abilities (Shinoda et al., 1963). Surfactants, detergents, colloidal electrolytes, etc., can generally be represented by the symbolic formula RX , where R is the oleophilic moiety, and X is the hydrophilic moiety. The cationic portion of the surfactant molecule are mostly derived from substituted ammonium compounds, while the X part of the surfactants molecules are usually SO_3H^+ , OSO_3Na^- or CO_2Na^- , and ampholytes such as amino acids, and nonionic constituents ranging from glycerides, glucosides to polyoxyethylene and polyoxypropylene derivatives (Priyanto et al., 2001)

Surfactants even though exhibit a marked difference in structure, all possess the amphoteric tendencies to be oil soluble on one hand and water soluble on the other. Surfactants are commonly very surface active in aqueous solution, depressing the surface tension of water against air to about 25 dynes/cm at concentrations as low as 10^{-4} to 10^{-2} molar. Nonionic compounds tend to be more strongly surface active than ionic compounds, which leads to an important phenomenon on surfactants referred to as the micelle formation. Critical micelle concentration values of nonionic surfactants are much smaller as compared to the ionic surfactant concentration values. Related to this micelle formation is the surface activity as determined from surface tension measurements of aqueous solutions involving surfactants (Priyanto et al., 2001; Shinoda et al., 1963 and Lobanov et al., 1997).

A micelle may consist of two or three molecules or ions, or as many as several millions. Micelles in surfactant are not present at all concentrations. Below the critical concentration, the solute is present as single molecules or ions, and the micelles begin to form above a particular concentration. The changes in properties of surfactants, which occur as micelles form, are characterized by sudden transitions in many physical quantities such as: surface tension, viscosity, and conductivity.

Micellization is initiated by the hydrophobic and hydrophilic imbalance in surfactants. The hydrophobic part of the surfactant molecule tends to avoid contact with water or the aqueous solution, while the hydrophilic ionic head group tends to be strongly hydrated (Shinoda et al., 1963). The micellization of surfactant molecules can be explained as a compromise formed between the two different properties of the surfactant molecules.

Research findings have recently favored surfactants usage in wettability alteration. However, the economics of the process sometimes makes it unattractive, but the prevalent prices of oil are fastly changing this scenario in favor of surface active agents (surfactants). Surfactant induced wettability alteration and its effect on spontaneous and forced imbibition is the main subject of this study. Li and Horne (2002), Spinler et al. (2000) independently studied spontaneous imbibition of aqueous surfactant solution into preferentially oil-wet carbonate cores. They observed that chemical reaction takes place between the rock and the adsorbed polar organic components or carboxylates in the surfactant which alters wettability. Spinler et al. (2000) also observed that the onset of precipitation, cloud point formation in surfactants and increase in surface tension are measures of surfactant instability. They concluded that oil recovery can be improved with

low concentration of surfactant for both spontaneous and forced imbibition of water and that reduction in rock surface adsorption is achievable by reducing surfactant concentration below CMC. However, the uniformity of wettability alteration within an entire reservoir is still unclear. This surfactant/rock surface interaction has also been investigated by Standnes and Austad (1999) and their results corroborated with earlier findings. An analytical model was developed by Hognesen et al., (2004) to numerically test the findings of the investigations on effects of surfactants on carbonate surfaces and spontaneous imbibition of aqueous surfactant into preferentially oil wet carbonates. It was observed that gravity forces played a very important role in the fluid flow mechanism, while Standnes and Austad (1999) observed that wettability induced by crude oils on chalk surfaces is related to the amount of acidic components in the crude oil, and that surfactants of the tetra alkyl ammonium dissolved in water are able to irreversibly change the wettability of chalk by desorbing organic carboxylates. They described the imbibition mechanism as an interaction between surfactant monomers and adsorbed organic carboxylates from crude oil. It was also observed that changes in temperature, during surfactant wettability alteration process has a great impact on imbibition rates due to changes in interfacial tension (IFT), critical micelle concentration, and fluid viscosity.

Spinler et al. (2000) investigated spontaneous counter-current imbibition on North Sea reservoir chalk plugs. They observed that the core's wettability was moderately altered to water-wet at ambient temperatures. With the usage of low concentration surfactants, the oil recovery improved for spontaneous and forced imbibition. Their findings were interpreted to be a surfactant induced imbibition by wettability alteration.

Li et al. (2003) observed that counter-current imbibition is proportional to the interfacial tension (IFT) of two immiscible liquids and, this also depends on integral of the mobility along the invaded portion of the core and that the pressure of the nonwetting phase in the dead-end space ahead of imbibition front is constant for a short time after the onset of imbibition. Li et al., (2003) also observed that capillary back pressure associated with production of nonwetting phase at the open face of test core, is constant during frontal flow, this is interpreted to mean a drainage production mechanism at the open face.

Zhang et al. (2004) conducted spontaneous imbibition studies on oil-wet dolomite cores. They observed that there was no spontaneous imbibition on the cores for 8 months, but with the addition of an alkaline surfactant solution, spontaneous imbibition was initiated at approximately one hour after the commencement of the experiment. They reported that their scaled oil recovery curves showed that the process was dominated by gravity.

Ayirala and Rao (2004) studied beneficial effects of wettability altering surfactants in oil-wet fractured reservoirs. They proposed a “diffusion and imbibition” sequential process for wettability alteration. The surfactant in fractures diffuses into the rock matrix and alters wettability, enabling imbibition of more surfactant into the matrix, the repetition of this sequential process of initial diffusion followed by imbibition enables a near uniform wettability alteration within the rock matrix and enhances the recovery of oil.

2.8.3 Effects of Temperature and Pressure on Imbibition

Schembre et al. (1998) conducted investigations to determine effect of elevated temperature (45-230°C) and pressure (sufficient to maintain water as liquid water at these

temperatures) on imbibition and wettability alteration using diatomaceous reservoirs core samples with low permeability and high porosity. They observed an increase in imbibition rate and extent of oil recovery with increasing temperature. A remarkable shift in the wettability index of the core sample from intermediate and weakly water-wet to very strongly water-wet was noted. Also, a reduction in residual oil saturation due to enhanced production from spontaneous imbibition was observed. Rao (1999) studied wettability effects in thermal recovery operations using single-crystal and dual-crystal contact angle techniques. He observed that the quartz surface (in contact-angle tests) and sand surface (in core floods) exhibited shifts from strongly water-wet to strongly oil-wet state at high temperatures. He concluded that temperature dependence of wettability is affected by several factors such as pH, temperature effect on electrokinetic properties of hydrocarbon-water and solid-water interfaces, and brine composition. Another major observation in the studies was the precipitation of calcium carbonate out of the synthetic brine as the temperature of the contact angle cell was raised. The precipitated calcium carbonate deposits render host surfaces strongly water-wet.

Tang and Morrow (1999) demonstrated that an increase in temperature in sandstones always resulted in increased water wetness, which improves spontaneous imbibition of water and hence increased oil recovery. A similar observation was recorded for North Sea carbonate rocks. In the investigation, it was noted that Amott Index increased with temperature. Zhou et al. (1996) also observed that imbibition rate decreases in sandstones as the core aging time increases. This is attributed to onset of mixed wettability of core, arising from the adsorption of polar components in crude oil, during the immersion of core in oil under high temperature and pressure.

Tang and Kovscek (2002) observed that oil saturation remaining after spontaneous water imbibition into field and outcrop core samples decreases as temperature is increased. To explain temperature effect on wettability, Blunt and Al-Hadrami (2001) proposed a model to show that wettability alteration at elevated temperatures is due to direct desorption of asphaltene macromolecules from rock surfaces. They assumed a critical temperature whereby asphaltene on rock surface is spontaneously desorbed, hence the desorption reverts rock surfaces to water-wet surface which improves spontaneous imbibition of water and improves production.

2.9 Concluding Remarks on Reviewed Literature

The importance of imbibition in oil recovery from reservoir has been extensively studied. These research studies show that several factors such as temperature, wettability, IFT, viscosity ratio, pressure and capillary forces affect imbibition. Spontaneous imbibition appears to be the dominant production mechanism for many naturally fractured reservoirs. The wettability of a medium has a direct link with imbibition rates. Spontaneous imbibition is more readily observed in water-wet media. The wettability of a medium can be altered from oil-wet to water-wet to improve spontaneous imbibition and hence higher oil recovery (Rao and Ayirala, 2004).

Almost all imbibition studies have been conducted in the laboratory and were scaled to the field by analytical methods (Akin and Kovscek, 1999). Much investigation emphasis has been placed on carbonaceous rocks, due to the importance of the North Sea chalks and West Texas carbonates. Morrow and Mason (2001) observed that the establishment of a single imbibition study, forced or spontaneous, co-current or countercurrent which will be representative of all reservoirs is impossible. Detailed

imbibition study of reservoirs, advances in understanding of Crude/Oil brine rock interactions will be of a immense help in reservoir recovery and predictive capabilities. They further concluded that good simulation of imbibition recovery mechanisms, rate and efficiency, dynamic saturation profiles arising from production and capillary data will continue to serve as the major tool for the improvement of the predictive capabilities and a major requirement in the understanding of reservoir mechanics.

Sufficient open literature was not available to show the major field investigations of spontaneous and forced imbibition, even though they are the dominant production mechanisms. However, imbibition is a naturally occurring phenomenon in fractured reservoirs and the laboratory investigations conducted on cores from the field were scaled to represent the expected field results. Spontaneous imbibition has been identified to be a major production mechanism of some North Sea reservoirs such as Ekofisk, Middle Eastern reservoirs and West Texas carbonate reservoirs.

CHAPTER 3

EXPRIMENTAL APPARATUS AND PROCEDURE

3.1 Objectives and Reagents Used

The main aim of this research investigation is to experimentally determine the Yates rock wettability alteration at reservoir conditions using live oil and also quantify wettability indices associated with the wettability alterations caused by surfactants using the Amott wettability measurement method.

Since coreflood investigation was carried out at reservoir conditions, Yates live oil was used in the corefloods while the Yates stock tank oil was used in the ambient-condition imbibition tests. Yates field synthetic brine was prepared in the laboratory with high quality salts manufactured by Fisher Scientific. Deionized water was obtained from Water Quality Laboratory at Louisiana State University. Yates crude oil, nonionic surfactant (ethoxy alcohol) and anionic surfactant (ethoxy sulphate) were provided by Marathon Oil Company. The stock tank oil provided was used to prepare live oil by adding lighter ends contained in original Yates field live oil. The volumes of lighter components to be added were computed from Yates live oil composition provided by Marathon Oil Company. The crude oil was securely protected from oxidation by keeping it under a Nitrogen blanket. The synthetic brine, filtered with Sterivac TM was used to prepare the different concentration of the surfactant for the investigation.

3.2 Yates Live Oil Preparation

Yates synthetic live oil is prepared according to the Yates reservoir oil composition. This is done by calculated additions of the light constituents (C1 – C5) to Yates stocktank oil at Yates reservoir pressure of 700 psi and temperature, 82 °F and rocking the live oil

cylinder 16 – 18 hours for good mixing and attainment of a single oil phase with dissolved gas. The light end constituents were added in proportions or volumes after a detailed analysis of the Yates reservoir fluid has been carried out as shown in Table 1. All additions of fluids were performed at pressure above the Yates field reservoir pressure and the synthetic live oil was kept at pressure above the Yates field bubble point pressure of 680 psi.

Table 1: Composition and Properties of Yates Live Oil (Rao and Xu, 2005)

Component	Molecular Weight	Live Oil Mole fraction	Z Factor	Density g/cc	Pressure		Volume Added cc gas/mol Live Oil
					kPa	psig	
N ₂	28.000	0.012013	0.9873	---	3500	508	8.521
CO ₂	44.100	0.053261	---	0.7399	6895	1000	3.174
C ₁	16.010	0.092727	0.7993	---	20685	3000	9.010
C ₂	30.100	0.035863	---	0.3644	6206	900	2.962
C ₃	44.090	0.021439	---	0.5277	1400	203	1.808
C ₄	58.120	0.035741	---	0.6084	700	102	3.414
C ₅	72.146	0.027104	---	0.6262	89	13	3.123
C ₆₊	245.141*	0.721846	---	0.8779	3447	500	201.565**
Total		1.000000					233.577
* Analyzed by a commercial laboratory. ** Volume of Stock Tank Oil per Mole of Live Oil.							

3.3 Experimental Setup

The Hassler type core holder equipment was used to carry out all the reservoir condition investigations. Figure 4 shows the system assembly for the reservoir condition investigation. It shows the live oil, brine vessels and the core holder. This core holder is rated to 10,000 psi and a temperature of 400 ° F. The Yates reservoir temperature was approximately 80° F. A heat strap with temperature adjustment provision and

thermometer were used to keep temperature constant throughout the investigation period. The entire core flooding system consisted of (1) a Ruska pump for injecting fluids into the core, (2) a pressure gauge to measure the pressure drop across the core during core floods, (3) core rubber sleeve which protects the core in the core holder and applies uniform overburden pressure to the core, (4) Hassler type core holder, (5) a measuring cylinder (separator) to measure the flow rates and fluid volume at the outlet of fluids produced from the core. The dead volume of fluids in some portions of the flowlines were measured and accounted for in all the material balance calculations for saturations. A graduated imbibition flask was used for the Amott wettability tests, to measure volumes of fluids spontaneously imbibed into the core.

3.4 Experimental Procedure

The coreflood apparatus is used to determine oil recovery, saturations of oil, brine and end-point effective permeabilities. Synthetic brine matching the Yates reservoir brine composition was used in all the investigations conducted for this research. A coreflood simulator uses the data from the experiments to estimate oil/water relative permeabilities. The simulator used in this investigation uses the JBN technique (Okazawa, 1983) which is able to analyze coreflood data without capillary pressure data to yield oil-water relative permeabilities.

The core flood apparatus is also used for forced imbibition investigations. Yates core is placed in the imbibition flask for spontaneous oil or water imbibition for an approximate time of two weeks. The amount of fluid spontaneously imbibed by the core is noted and the core is then retrieved from the imbibition flask and installed in the core

holder for forced imbibition studies. The series of experiments conducted during this investigation are shown in Table 2.

Table 2: List of Experiments Conducted for Wettability Alteration Study

Set	Investigation Mode	Surfactant	Oil	Core Properties			
				L (cm)	D (cm)	K (mD)	ϕ (%)
1	Coreflood	Nonionic	Yates Live Oil	8.890	3.81	765	31.30
2	Coreflood	Anionic	Yates Live Oil	8.890	3.81	768	32.22
3	Imbibition	Nonionic	Yates Stock tank Oil	8.890	3.81	768	32.22
4	Imbibition	Anionic	Yates Stock tank Oil	8.890	3.81	768	32.22

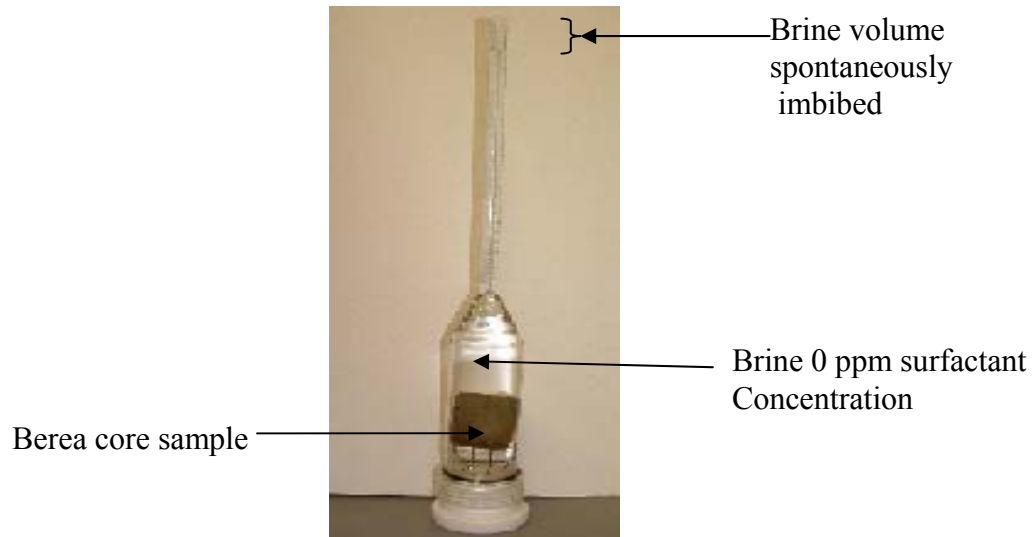


Figure 3: Imbibition Flask with Core under Spontaneous Imbibition

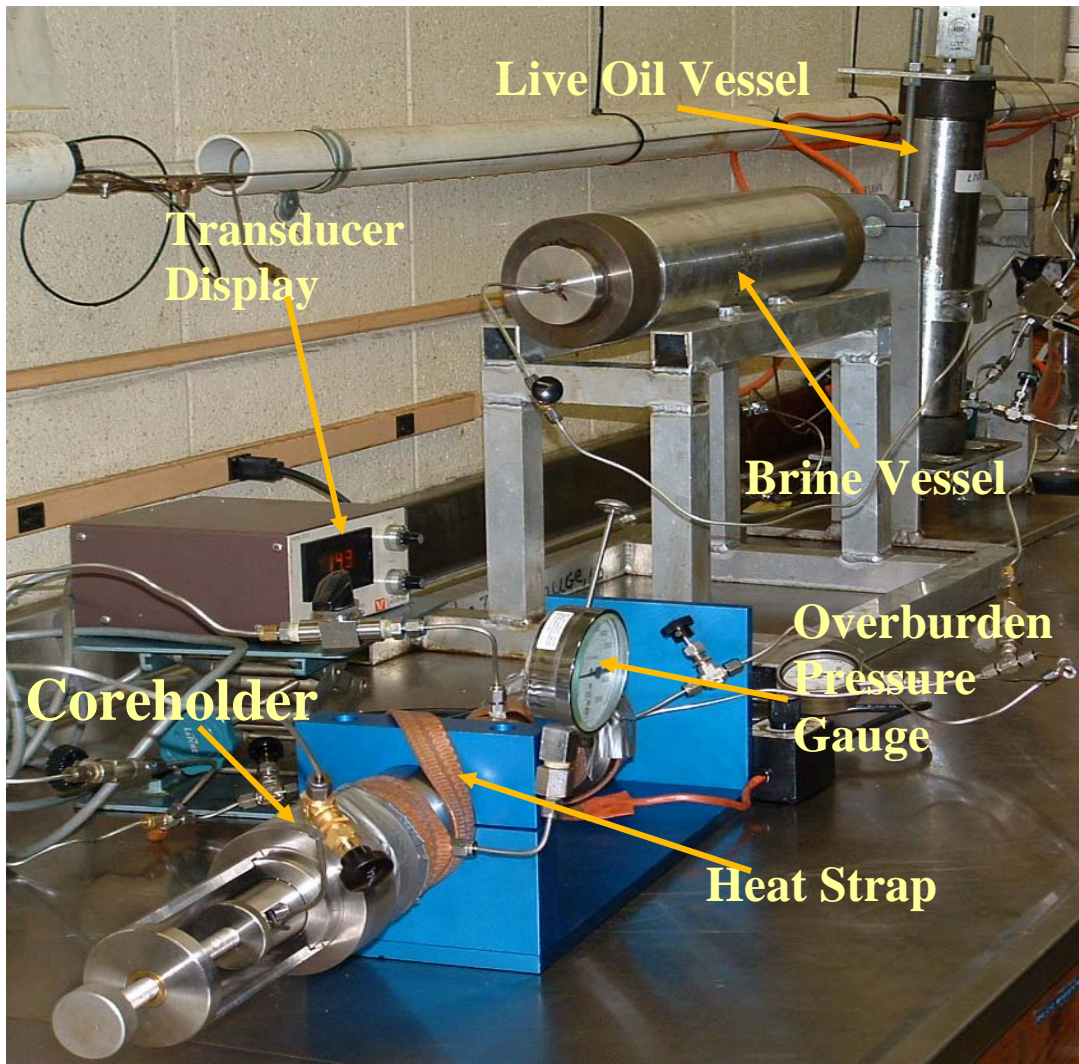


Figure 4: Core Flood (Forced Imbibition) System Used in this Study

Yates synthetic brine and Yates field core were used for the experiments conducted in this research study. Figure 3 shows a vacuumed sample of Berea core undergoing spontaneous imbibition for determination of pore volume measurement, while Figure 4 shows the coreflood system used for the wettability alteration investigation at reservoir conditions. The cores used in this study were obtained from Yates field at 1,558.86 m (5,114.62 ft) to 1,560 m (5,118.36 ft) depth. Five sets of experiments were conducted for each of the surfactants used. The surfactant

concentrations used were 0, 500, 1500, 3500 and 5000 ppm. Total floods conducted were 19 (5 corefloods each for non-ionic and anionic surfactant, 5 corefloods for forced imbibition using non-ionic surfactant and 4 corefloods for forced imbibition using anionic ethoxy sulphate surfactant).

All investigations were conducted on Yates field cores with similar sizes and core properties. The surfactant concentrations used in the investigation were adapted from field operations. Leas and Rappaport (1953) linear coreflood criterion ($LV\mu \geq 1.0$) was used to calculate the minimum stable volumetric flow rates to be used in each of the experiments to ensure all the floods are stable and recoveries are not dependent on injection flow rate. Same criterion was used for the forced imbibition process.

Before commencement of investigation, the core was saturated with brine to determine its porosity and the absolute permeability. Then stock tank oil was injected at a rate of 1.5cc/min for 5 pore volumes and live oil flooding was carried out for 2 pore volumes to bring core to initial water saturation (S_{wi}). The core was allowed to age for 2 weeks (14 days) under reservoir conditions and overburden pressure of 1000 psi was applied to the core during aging time and when the floods were being conducted. The core was then brought back to S_{wi} flooding with oil. The effect of surfactant concentration on oil recovery was studied by carrying out several floods with synthetic brine containing pre-selected varying surfactant concentrations (500, 1500, 3500 and 5000 ppm). These concentrations were used for both surfactants (ethoxy alcohol and ethoxy sulphate). The pressure drop across the core along with brine and oil productions were continuously monitored during all coreflood experimental investigations conducted. A coreflood simulator was used to calculate oil-water relative permeabilities by history matching the

pressure drop and the recovery data for each of the coreflood conducted. These relative permeability data have been used to interpret changes in wettability brought about by the surfactant solutions at varying concentrations.

3.5 Imbibition Experiments

Imbibition tests for the determination of the Amott wettability index (I_w) was conducted with the linear coreflood equipment, the Hassler core holder and the imbibition flask. The coreflood equipment was used for forced imbibition determination and the flask was used to measure the spontaneously imbibed oil or water. The Amott wettability procedure, with some little modification was used for the Yates field imbibition tests.

The test procedure is commenced by installing the core in a core holder and vacuuming core to at least -1 bar using the vacuum pump and gauge provided in the laboratory. The pore volume of the core is then measured by using the Ruska pump. The core is cleaned by using the sequential cleaning procedure of flowing 2 pore volume of Yates brine through the core followed by 2 pore volume of diluted Yates brine (50% brine and 50% deionized water), 2 PV Isopropyl alcohol followed by 2 PV toluene solvent. The process is repeated in a reverse manner by flooding 2 PV Toluene solvent followed by 2 PV of Isopropyl alcohol, 2 PV of diluted Yates brine and finally 4 PV of Yates brine. The flooding rate for all cleaning fluids is 120cc/hr. The core is assumed to be 100 % brine saturated after the cleaning process. Oil flood is carried out for a total of 3 PV at 90cc/hr flood rate to bring core to irreducible water saturation (S_{iw}). Brine flood is then carried out to establish residual oil saturation (S_{or}) for the core. The Amott wettability test steps enumerated in detail in Chapter 2 (section 2.7.1) is then followed step by step measure the index. These steps are followed for all surfactant concentrations.



Figure 5: Imbibition Flask Showing Yates Core and Oil Produced by Spontaneous Imbibition of Yates Brine at 1500 ppm Ethoxy Alcohol Surfactant Concentration.



Figure 6: Imbibition Flask Showing Yates Core in Oil and Brine Produced by Spontaneous Imbibition of Yates Oil.

3.6 Coreflood Simulation for Determination of Oil-Water Relative Permeabilities

A semi-analytical relative permeability model developed by Okazawa (1983) was used to simulate the coreflooding experiments. The model was developed for application in cases in which capillary pressure data were unavailable.

The model works by iteratively finding the values of corey exponents (e_o and e_w) by minimizing the sum-of-squares of the weighted deviations of the experimental pressure and production histories from the calculated values. The following functions are used to generate the relative permeabilities from coreflood data:

$$K_{rw} = S_w^e \cdot K_{rwm} \quad (13)$$

$$K_{ro} = (1-S_o)^e \cdot K_{rom} \quad (14)$$

$$S = (S_w - S_{wi}) / (S_{wm} - S_{wi}) \quad (15)$$

Where K_{rw} is the relative permeability to brine, K_{rwm} is the relative permeability to brine at S_{or} , K_{ro} is the relative permeability to oil and K_{rom} is the relative permeability to oil at S_{wi} , S_w is the brine saturation, S_{wi} is the irreducible brine saturation, S_{wm} is the maximum brine saturation (or $1 - S_{or}$), e_o and e_w are Corey exponents.

CHAPTER 4

RESULTS AND DISCUSSION

Laboratory experiments were conducted in this experimental study to determine surfactant induced wettability alteration of Yates field core samples. Previous surfactant induced wettability alteration experiments on similar cores as used in this study were conducted, using stock-tank oil at ambient conditions and at reservoir pressure and temperature (Sharma et al, 2005). Similar experiments were carried out using reactive system (Yates core + Yates synthetic brine + Yates stock tank oil) and non-reactive system (Berea core + Yates Synthetic brine + decane), (Ayirala, 2002) using surfactants.

A detailed summary of results for experiments conducted in this study is shown in Table 2. End-point relative permeabilities were measured for the system at various surfactant concentrations. The characteristics of relative permeability curves, initial water saturation, end-point relative permeabilities to water and oil and cross-over points were used to interpret surfactant induced wettability alterations.

Current investigation is focused on wettability alteration using Yates live oil (recombined Yates stock-tank oil) at reservoir conditions. The mechanism behind this process is reduction in interfacial tension as well as wettability alteration. A rule-of-thumb proposed by Archer (1971), Thomas (1971) and Craig (1971) adapted from previous investigations and wettability interpretation were used to interpret the wettability of the system and the comparison with stock tank oil floods at reservoir conditions (Table 3).

Table 3: Rules-of-thumb for Wettability Inference from Oil-Water Relative Permeabilities

S/No	Criterion	Water-Wet	Oil-Wet	Reference
1	End-Point Relative Permeability to Oil at S_{wi}	> 95%	< 70% - 80%	Archer Thomas (1971)
2	End-Point Relative Permeability to water at S_{or}	< 30%	< 50%	Craig (1971)
3	Water Saturation at Cross-over Point	> 50%	< 50%	Craig (1971)
4	Initial Water Saturation, S_{wi}	> 25%	< 15%	Craig (1971)

4.1 Effect of Nonionic Ethoxy Alcohol Surfactant on Wettability

The wettability altering investigations conducted using Yates live oil and Yates synthetic brine + ethoxy alcohol at 0ppm, 500ppm, 1500ppm, 3500ppm and 5000ppm surfactant concentrations showed an improvement in recovery of oil from the Yates reservoir core. These experiments were carried out at reservoir conditions (82°F and 700 psi). The results are presented in Table 4 and Figure 7. A gradual increment in oil recovery from 66% at 0 ppm surfactant concentration to a maximum recovery of 86% at an optimum surfactant concentration of 1500ppm was observed. The oil recovery subsequently declined to 81% and 71% at 3500 ppm and 5000 ppm surfactant concentration respectively.

Oil/water emulsions were observed during the coreflood experiments using ethoxy alcohol. The emulsion was more pronounced at higher surfactant concentrations (3500 ppm and 5000 ppm). This emulsion was persistent and did not break down even after long exposure. These emulsions hindered free flow of fluids in the flowlines and caused high pressure drops across the test core as measured by the transducer.

Table 4: Comparison Between Experimental and Simulator Results of Corefloods of Yates Live oil in Yates Reservoir core at various Nonionic Surfactant (Ethoxy alcohol) Concentrations

Conc (ppm)	Experimental					Simulator			
	Recovery (%OOIP)	Swi	Sor	Kro	Krw	Swi	Sor	Kro	Krw
0	66	0.276	0.243	0.513	0.136	0.239	0.227	0.382	0.100
500	70	0.348	0.194	0.555	0.235	0.300	0.178	0.580	0.163
1500	86	0.436	0.074	0.510	0.151	0.446	0.157	0.457	0.153
3500	81	0.483	0.094	0.303	0.129	0.430	0.151	0.485	0.139
5000	71	0.458	0.155	0.353	0.212	0.415	0.176	0.430	0.171

The high pressure drops observed caused low end-point oil permeabilities and thus hindered the applicability of the rules-of-thumb. The presence of emulsion is evidence by the stop-and-go shape of the production curves in figure 7 at surfactant concentration of 1500 ppm and higher. The relatively smooth production patterns at 0 and 500 ppm are indicative of the absence of emulsion formation and consequent flow blockage.

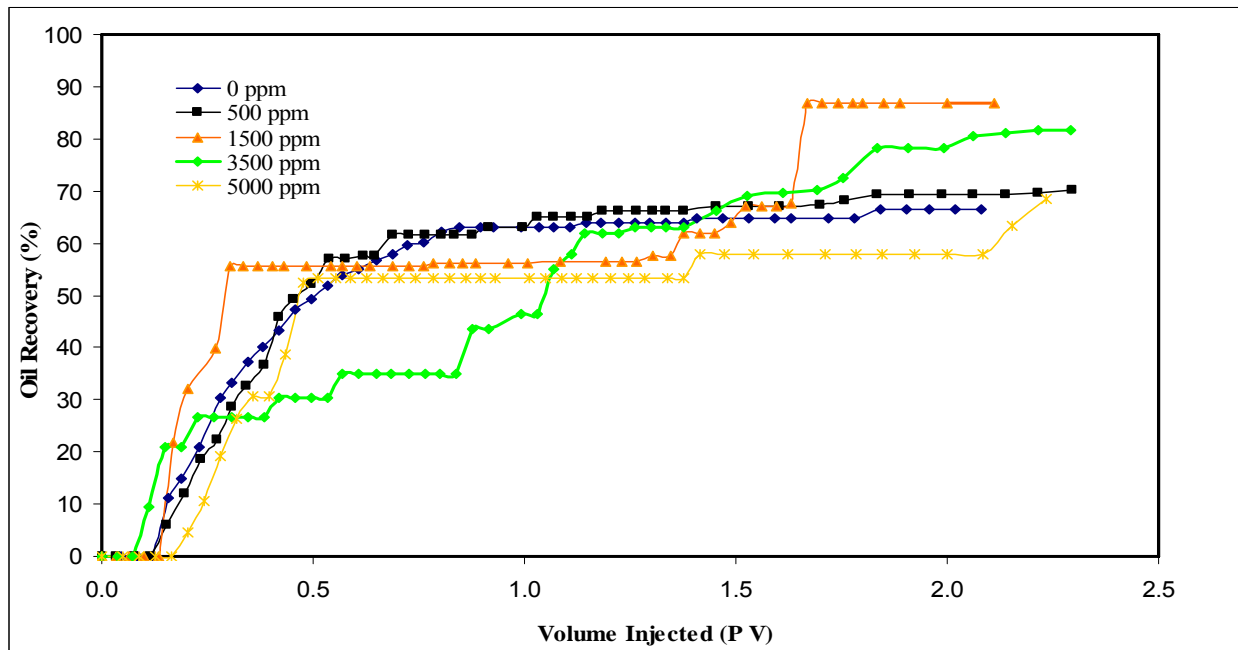


Figure 7: Oil Recoveries from Coreflood Using Yates Cores, Yates Live Fluids and Nonionic Ethoxy Alcohol Surfactant at Reservoir Conditions

Similar coreflood investigation conducted using Yates stock tank oil + Yates synthetic brine + ethoxy alcohol surfactants and Yates reservoir core at reservoir conditions, reported by Amit Sharma (2004) showed an increase in recovery with surfactant concentration. The results are given in table 5. Maximum recovery of 73% was observed at surfactant concentration of 3500ppm which differs from the optimum concentration of 1500 ppm observed in the live oil investigations.

The optimum concentration of ethoxy alcohol surfactant was not very clear in the investigation involving stock tank oil at reservoir conditions as 72% recovery was observed at 500 ppm and 1500 ppm while 73% recovery was observed at 3500 ppm concentration. The live oil investigations displayed a clear optimum surfactant concentration of 1500ppm and reasonable oil recovery values from the core. Lot of foaming was observed in the separator during the live oil investigations. The foams were observed to increase with the surfactant concentration. Foaming problems were minimal in the stock tank oil coreflood investigation compared to live oil investigations. The foams broke down in approximately 24 hours leaving clear oil and water phases in the separator.

The difference in optimum oil recovery between live oil floods and stock tank oil core flood investigations at reservoir conditions was 13% (73% recovery in stock tank oil and 86% recovery from live oil). Also the reason for the different optimum surfactant concentration of 1500ppm and 3500ppm in the live oil and stock tank oil investigations, respectively, may be attributable to the differences in viscosity and density of oil used in the investigation, as the Yates live oil and stock tank oil have viscosities of 5.6cp and 16.5cp respectively. Interestingly, optimum oil recovery was

observed to be 72% at 1500 ppm ethoxy alcohol nonionic surfactant concentration in stock tank oil corefloods at reservoir conditions.

Table 5: Comparison of Live Oil Floods with Stock Tank Oil Floods for Varying Concentrations of Anionic Surfactant at the Same Pressure (700 psi) and Temperature (82°F)

Expt	Live Oil Investigations					Stock Tank Oil Investigations				
	Recovery (%OOIP)	S_{wi}	S_{or}	K_{ro}	K_{rw}	Recovery (%OOIP)	S_{wi}	S_{or}	K_{ro}	K_{rw}
0 ppm	66	0.276	0.243	0.513	0.136	67	0.312	0.227	0.643	0.148
500 ppm	70	0.348	0.194	0.555	0.235	72	0.372	0.178	0.579	0.163
1500 ppm	86	0.436	0.074	0.510	0.151	72	0.435	0.156	0.457	0.153
3500 ppm	81	0.483	0.094	0.303	0.129	73	0.435	0.151	0.487	0.139
5000 ppm	71	0.458	0.155	0.353	0.212	65	0.493	0.176	0.433	0.181

Table 5 shows a gradual increase in the irreducible water saturation (S_{wc}) in the live oil investigation from 27.6% at 0 ppm surfactant to 34.8% at 500ppm flood and 48% at 3500ppm. End-point relative permeabilities to oil and water measured at the end of each of experiment are also shown in Table 5. The relative permeabilities were affected by the effects of oil/water emulsion formed during the coreflood experiments on the pressure drop measured across the core. It was observed that these emulsions did not break down for up to 72 hours, and sometimes even longer after the conclusion of the experiment. The history match of pressure drop and recovery results from the simulator for 0ppm to 5000 ppm ethoxy alcohol surfactant concentration are shown in the appendix Figure A1 to A5. The resulting relative permeability characteristics obtained from the simulator for live oil investigations at various surfactant concentrations as shown in Figure 8 on next page, For 0 ppm surfactant concentration, (Figure 8(a)), $S_{wi} = 27\% > 25\%$, $K_{rw} = 13\% < 30\%$ and $S_{w,c-o} = 66\% > 50\%$ indicate water-wet nature. However, K_{ro} of $51\% < 70\%$ indicates oil-wet characteristics.

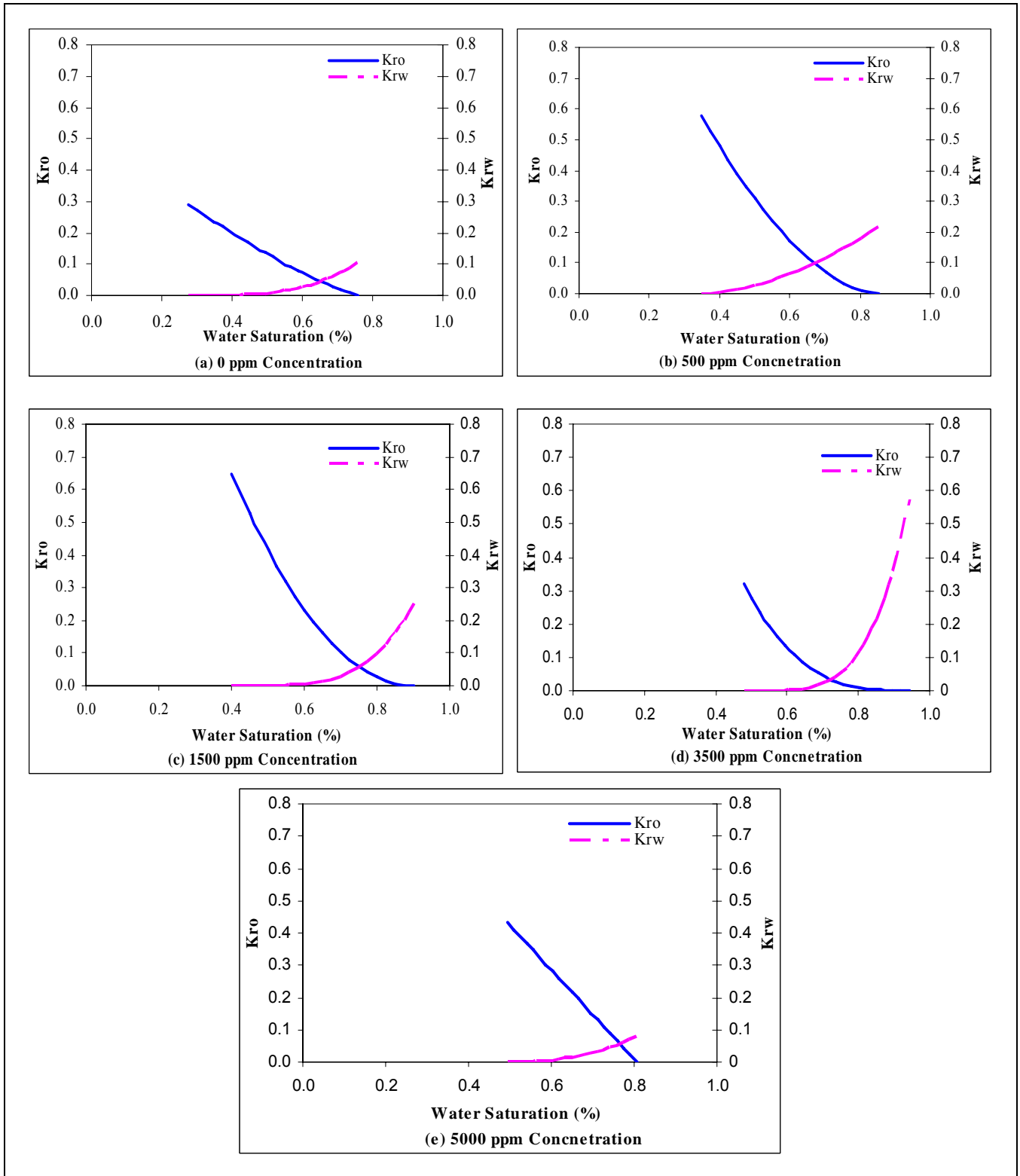


Figure 8: Relative Permeability Simulator Output of Yates Core and Live Oil at Reservoir Conditions with Nonionic Ethoxy Alcohol Surfactant at Various Concentrations

Relative permeability curves at 500 ppm ethoxy alcohol surfactant concentration (Figure 8(b)) indicate water-wet characteristics ($S_{wi} = 31\% > 25\%$, $S_{w,c-o} = 58\% > 50\%$, $k_{rw} = 23\% < 30\%$). The end-point oil relative permeability of 55% maybe attributable to formation of emulsions.

Relative permeability curves at 1500 ppm surfactant concentration (Figure 8(c)) indicate water wet/ mixed wet characteristics ($S_{wi} = 38\% > 25\%$, $S_{w,c-o} = 75\% > 50\%$, $k_{rw} = 15\% < 30\%$). However, k_{ro} of 51% $< 70\%$ again indicates oil wet characteristics.

Relative permeability curves at 3500 ppm surfactant concentration (Figure 8 (d)) indicate water wet/ mixed wet characteristics ($S_{wi} = 40\% > 25\%$, $S_{w,c-o} = 71\% > 50\%$, $k_{rw} = 12\% < 30\%$). k_{ro} of 35% $< 70\%$ again indicates oil wet nature of Yates core at this surfactant concentration.

Wettability interpretations can be obtained from relative permeabilities in a similar manner even for 5000 ppm surfactant concentration (Figure 8(e)).

Other important observations made in this investigation using the Yates live oil + ethoxy alcohol surfactant + Yates synthetic brine are summarized as follows;

1. The enhanced oil recovery obtained at 0-1500 ppm concentration of non-ionic ethoxy alcohol surfactant at Yates reservoir conditions may be attributable to wettability alteration. This was however reversed at higher concentrations of the ethoxy alcohol surfactant. Emulsion formation was also noticed at the higher concentrations of the surfactant.
2. The initial water saturation was observed to increase gradually as the concentration of the surfactant was increased from 0 ppm to 5000 ppm. The initial

- water saturation was greater than 25 % for all the floods which indicates a water wet characteristic of the core based on Craig's rules (Craig 1971).
3. The end-point relative permeability to water at residual oil saturation were all less than 30 %, with the highest value observed for the 500 ppm flood. Their values suggested water wet tendencies for the Yates core, again from Craig's rule.
 4. A major shift to the right was observed for the water saturation crossover-point from 66% to 75% at 0 ppm and 1500 ppm surfactant concentration respectively. This trend was reversed for higher surfactant concentration of 3500 ppm and 5000 ppm where crossover points are 71 % and 69 % respectively. This crossover point shift resulted in higher oil recovery from the Yates core at an optimum surfactant concentration of 1500 ppm. It appears that a mixed wettability condition as previously discussed in chapter 2 of literature review was attained at this anionic ethoxy alcohol surfactant concentration. The recovery at this surfactant concentration was the optimum and the relative permeability ratio curves as well as the fractional flow curve show the greatest rightward shift, which is believed to be associated with mixed wettability conditions.
 5. End-point relative permeability to reservoir oil at initial water saturation gradually decreased from 55 % to 35% in the floods as non-ionic surfactant concentration is increased from 0 ppm to 5000 ppm. This drop in end-point oil permeabilities may be interpreted as a wettability shift.
 6. The relative permeability ratios obtained for nonionic ethoxy alcohol surfactant shown in Figure 8, gradually shifted from left to right at 0 through 1500 ppm non-ionic surfactant concentration. This trend was reversed to a leftward shift at 3500

ppm and 5000 ppm surfactant concentration. The leftward shift may be as a result of formation of emulsions as was also observed by Ayirala (MS thesis, 2002).

As previously mentioned, emulsion formation has profound influence on end-point relative permeabilities due to high pressure drops. Hence they cannot alone be used to infer wettability. Therefore shifts in relative permeability ratio curves (k_{rw}/k_{ro}) were also used to infer wettability alterations. The (k_{rw}/k_{ro}) plot for the live oil investigation is shown in Figure 8. The figure shows a rightward shift of the relative permeability ratios at relative permeability ratio of 1 ($k_{rw}/k_{ro}=1$). The band of the relative permeability ratio curves are also longer and wider at surfactant concentration corresponding to higher recoveries, for example, the band extend from 40% to about 92% water saturation or 8% to 60% oil saturation.

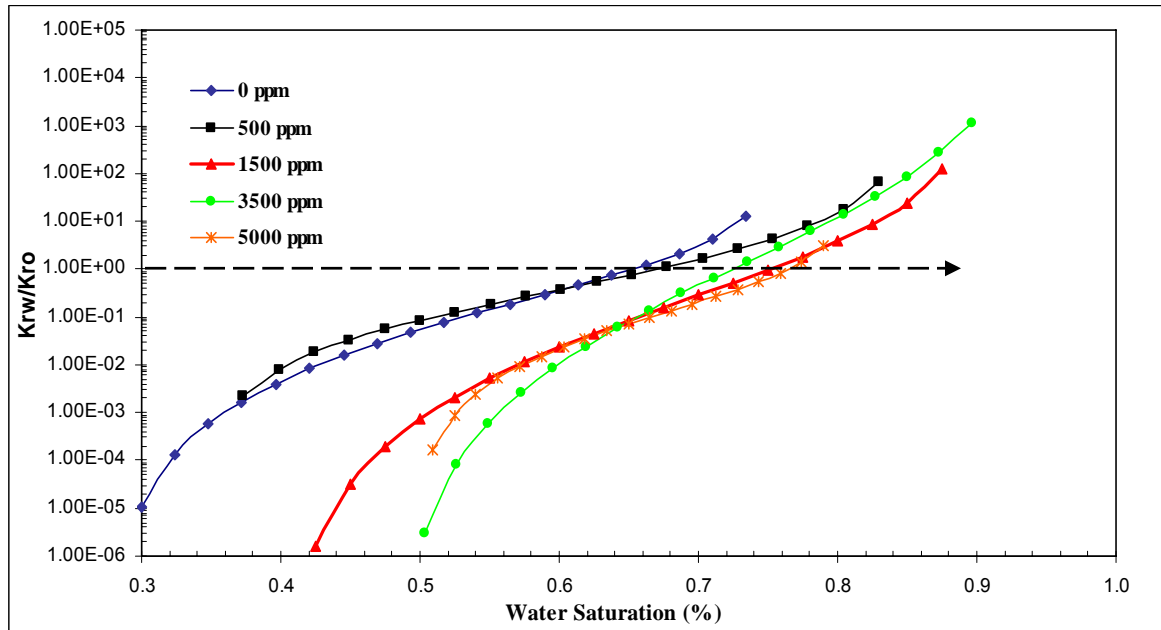


Figure 9: Coreflood Simulator Results of Relative Permeability ratios at various Nonionic Ethoxy Alcohol Surfactant Concentrations for Yates Reservoir Rock Live Fluids at 82°F and 700 Psig

4.2 Application of Fractional Water Flow to Wettability Alteration

A detailed summary of results for experiments conducted in this study, using ethoxy alcohol surfactant were shown in Table 4. End-point relative permeabilities were determined at various surfactant concentrations using a relative permeability simulator. The characteristics of relative permeability curves, initial water saturations, end-point relative permeabilities to water and oil were used in the previous section to interpret surfactant induced wettability alterations. The resulting fractional water flow curves computed for various surfactant concentrations are given in Figure 10. The figure shows a gradual shift to the right of fractional water flow curves to the right as surfactant concentrations increase from 0 ppm through 1500 ppm.

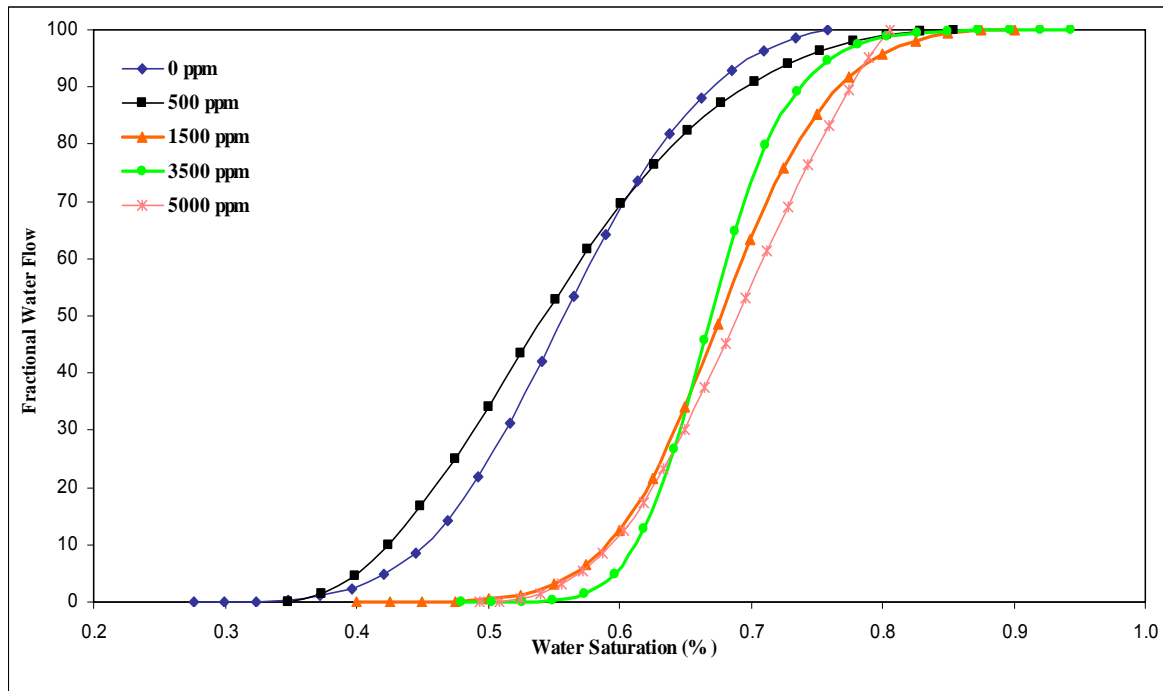


Figure 10: Effect of Nonionic Ethoxy Alcohol Surfactant Concentration on Fractional Water Flow

Using the viscosity data of the displacing and displaced fluids, the fractional water flow equation shown below and the derivative (equation 14) are used to estimate

the fractional water curves for the floods at different saturations and different surfactant concentrations.

$$f_w = \frac{1}{1 + \frac{\mu_w K_{ro}}{K_{rw} \mu_o}} \quad (13)$$

$$f_w' = \frac{df_w}{dS_w} = \frac{f_{wf} - f_{wi}}{S_{wf} - S_{wi}} \quad (14)$$

Here, f_w' is fractional water flow derivative with respect to water saturation, f_{wf} is fractional water flow at the front, f_{wi} is initial fractional flow, S_{wf} is water saturation at the front, μ_o and μ_w are viscosities of oil and water, K_{ro} and K_{rw} are relative permeabilities to oil and water, respectively.

Using the optimum ethoxy alcohol surfactant concentration of 1500 ppm, and lower 500 ppm surfactant concentration, shock front and frontal saturation was estimated for both concentrations of ethoxy alcohol on recovery. The average water saturation at the shock front for both floods were estimated using the fractional water flow curve tangential approach for estimation of shock front and average frontal water saturation (Willihite, 2004) shown in Figures 12 and 13.

The average water saturation ($\overline{S_w}$) for 500 ppm flood is 0.73 while that for 1500 ppm flood is 0.81. This analysis has further helped to explain the reason for the higher recovery associated with the optimal surfactant concentration as shown in Table 5 where oil recovery obtained for the 1500 ppm flood is 86% compared to a recovery of 70% for the 500 ppm surfactant flood. This increase in recovery may be attributable to wettability alteration.

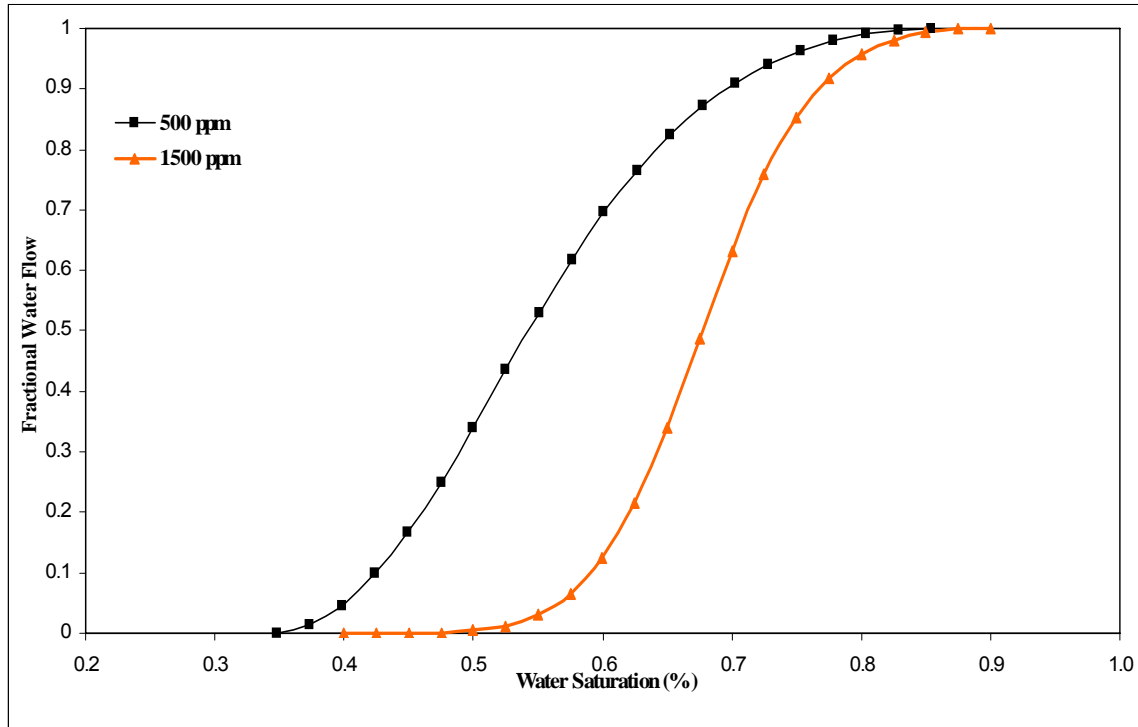


Figure 11: Fractional Water Flow Curve for 500 ppm and 1500 ppm Ethoxy Alcohol Surfactant Floods.

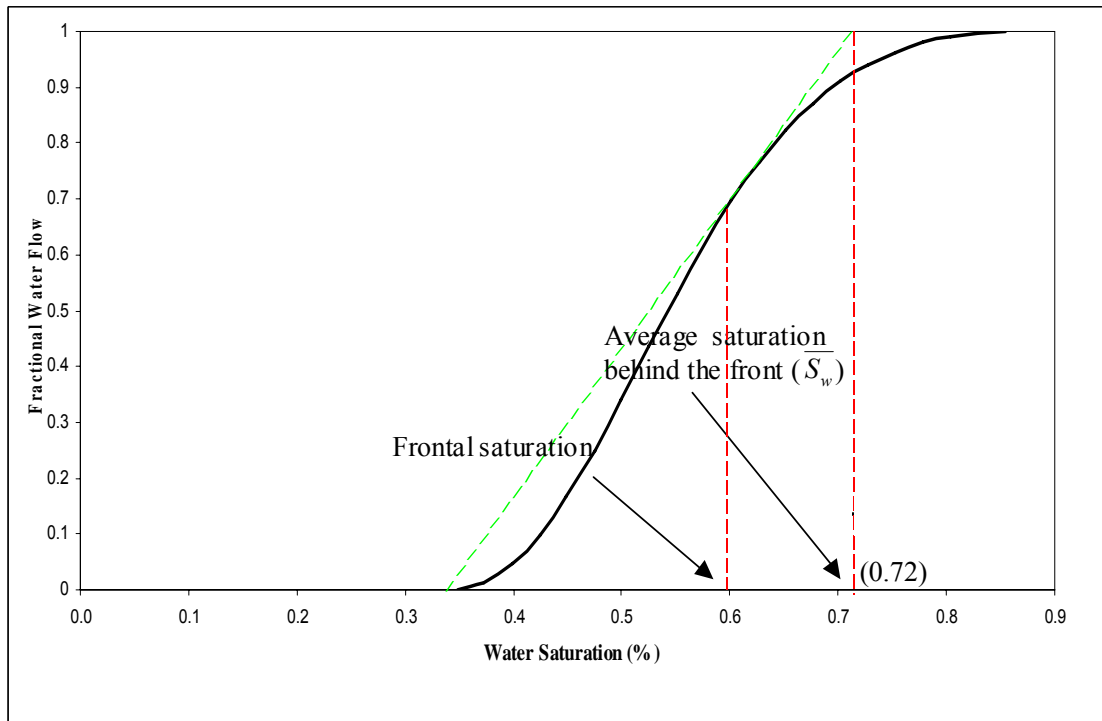


Figure 12: Fractional Water Flow Curve and Average Saturation Tangent for 500 ppm Surfactant Flood at Reservoir Conditions.

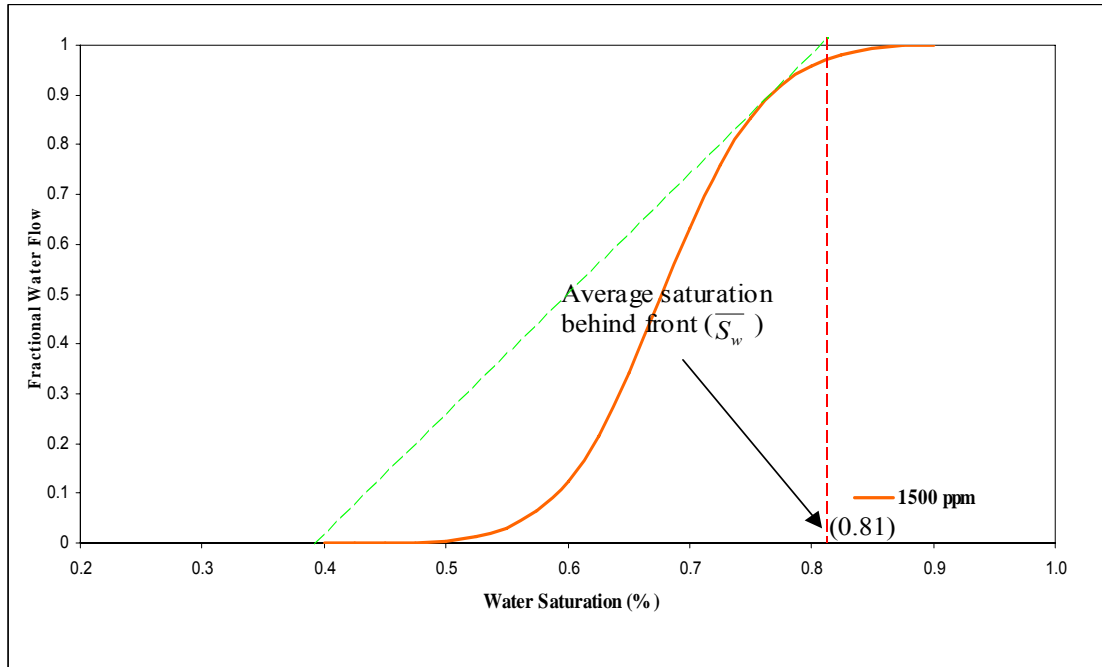


Figure 13: Fractional Water Flow Curve and Average Saturation Tangent for 1500 ppm Surfactant Flood at Reservoir Condition.

A higher average water saturation ($\overline{S_w}$) behind the shock front of the optimal surfactant concentration of 1500 ppm corresponds to higher recovery.

The relative permeability ratio curves as shown earlier in Figure 9 are gradually shifting to the right as the surfactant concentration is increased. For an initial water wet system, such type of gradual shift to right in the relative permeability ratio curves indicates the development of mixed wettability condition (Salathiel, 1973), (Ayirala and Rao, 2004). This is further substantiated with steady increase in initial water saturation and decrease in residual oil saturations as the surfactant concentration is increased.

Xu and Rao, (2005) conducted extensive investigation on contact angle phenomena. They researched the effects of crude oil type (live oil and stock tank oil), temperature, pressure, brine composition and rock type on dynamic contact angle. The

investigations were carried out at Yates reservoir conditions as well as ambient conditions. They used the new dual drop dual crystal (DDDC) advancing contact angle measuring technique, since the measurement of a single static contact angle to characterize multiphase fluid interaction has been known to yield poor reproducibility. The wetting classification in the investigation was interpreted (after Anderson, 1986): $0^{\circ}\sim 70^{\circ}$, water-wet; $75^{\circ}\sim 115^{\circ}$, intermediate-wet; $115^{\circ}\sim 180^{\circ}$, oil-wet. They further defined contact angles of $55^{\circ} - 75^{\circ}$ as weakly water-wet and $115^{\circ} - 135^{\circ}$ as weakly oil-wet.

Investigations by Xu (2005) of contact angles corroborated the surfactant induced wettability alteration observed in this study. He observed a contact angle of $55^{\circ} - 60^{\circ}$ for Yates reservoir rock, Yates synthetic brine and live oil at reservoir conditions, which corresponds to an initially weakly water-wet native state. Corefloods conducted also indicated water wet tendencies for the Yates core at reservoir conditions in presence of live oil as shown by experimental and relative permeabilities to live oil and brine in Table 7. An angle of $154^{\circ} - 156^{\circ}$ was measured for the same core in presence of Yates stock tank oil fluids at ambient conditions. Table 6 below shows a summary of contact angles extracted from Xu (2005).

Table 6: Dynamic Contact Angle of Yates Live Oil at Reservoir Conditions and Yates Stocktank Oil (Xu and Rao (2005))

Surf Conc (ppm)	Live Oil Test		Stocktank Oil Test	
	Surf A	Surf B	Surf A	Surf B
	Contact Angle (θ)		Contact Angle (θ)	
0	55	55	154	154
500	65	140	154	136
1500	85	120	152	139
3500	82	135	152	140

Surf A (Nonionic Ethoxy Alcohol)

Surf B (Anionic Ethoxy Sulphate)

4.3 Effect of Anionic Ethoxy Sulphate Surfactant on Wettability

The wettability altering investigations conducted using Yates live oil and Yates synthetic brine + ethoxy sulphate surfactant at 0ppm, 500ppm, 1500ppm, 3500ppm and 5000ppm surfactant concentrations failed to result in favorable wettability alteration of Yates field. These experiments were carried out at reservoir conditions as before. Oil recovery was observed to decrease steadily from 76% at 0 ppm surfactant concentration to 47% at surfactant concentration of 5000 ppm respectively (Table 7 and Figure 13)

Table 7: Comparison of Experimental and Simulator Results of Yates Live oil in Yates Core at Various Anionic Surfactant Concentrations at Reservoir Conditions of 700 Psi and 82 °F

Case	Experimental					Simulator			
	Recovery (%OOIP)	Swi	Sor	Kro	Krw	Swi	Sor	Kro	Krw
Brine	76	0.147	0.238	0.543	0.134	0.146	0.381	0.446	0.289
500 ppm	65	0.229	0.299	0.334	0.248	0.229	0.399	0.564	0.103
1500 ppm	57	0.239	0.351	0.294	0.144	0.239	0.512	0.430	0.320
3500 ppm	47	0.276	0.385	0.290	0.227	0.275	0.543	0.430	0.350
5000 ppm	47	0.220	0.436	0.335	0.135	0.270	0.427	0.400	0.540

As with previous investigations involving nonionic ethoxy alcohol surfactant, oil/water emulsions were observed during the coreflood experiments using anionic ethoxy sulphate surfactant. In this case of the anionic surfactants, emulsion formed almost at all surfactant concentrations. This emulsion was persistent and did not break down even after 24 hours. The emulsions formed in this case were not as persistent as emulsions formed in the investigation involving ethoxy alcohol surfactants. These emulsions also hindered free flow of fluids in the flow lines and caused high pressure drops across the test core as measured by the transducer. The high pressure drops in turn caused low end-point oil permeabilities and thus hindered the application of Craig's

rules-of-thumb to interpret wettability state of the Yates core from oil water relative permeability data.

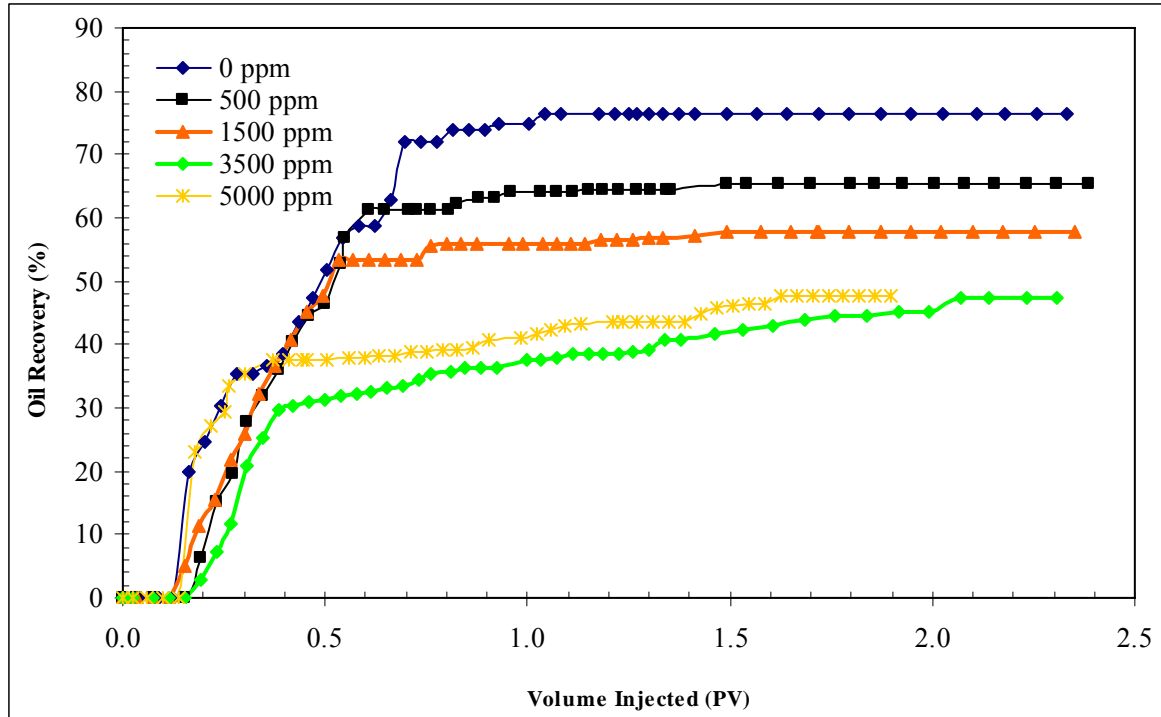


Figure 14: Oil Recoveries from Coreflood Using Yates Cores, Yates Live Fluids and Anionic Ethoxy Sulphate Surfactant at Reservoir Conditions

While the Yates live oil case showed a decreasing recovery trend with increasing anionic surfactant concentration, the Yates stocktank oil tests with ethoxy sulphate surfactants and Yates reservoir core at reservoir conditions, showed an increase in recovery with surfactant concentration as shown in Table 8. Maximum recovery of 72% was observed at brine surfactant concentration of 1500 ppm. Ethoxy sulphate surfactant, however, failed to show any appreciable increase in recovery in live oil floods.

Extensive foaming and emulsion formation relative to stocktank oil were observed in the separator during the live oil investigations using the anionic ethoxy sulphate surfactant. The emulsion severity was more than that noticed in the ethoxy alcohol

floods. The foam and emulsion formation were observed to increase with the surfactant concentration. Foaming problems were however, minimal in the stock tank oil coreflood investigation compared to live oil investigations. The foams broke down in approximately 24 hours and a clear oil and water phase were observed in the separator.

Table 8 compares the recovery and relative permeability data obtained from stock tank investigations to those conducted using live oil.

Table 8: Comparison of Live Oil Floods and Stock Tank Oil Floods Data Obtained at Reservoir Conditions of 700 Psi and 82°F for Varying Concentrations of Anionic Surfactant

Expt	Live Oil Displacements at Reservoir Conditions					Stock Tank Displacements at Reservoir Conditions				
	Recovery (%OOIP)	Swi	Sor	Kro	Krw	Recovery (%OOIP)	Swi	Sor	Kro	Krw
0 ppm	76	0.147	0.238	0.543	0.134	67	0.349	0.213	0.761	0.139
500 ppm	65	0.229	0.299	0.344	0.248	64	0.396	0.212	0.589	0.181
1500 ppm	57	0.239	0.351	0.294	0.144	72	0.483	0.143	0.687	0.464
3500 ppm	47	0.276	0.385	0.290	0.227	72	0.441	0.157	0.546	0.284
5000 ppm	47	0.220	0.436	0.335	0.135	63	0.407	0.218	0.470	0.248

Table 8 shows a gradual increase in the irreducible water saturation (S_{wc}) in the live oil investigation from 14.7% at 0 ppm flood to 22.9% at 500ppm oil flood and 27.6% at 3500ppm oil flood. End-point relative permeabilities to oil and water estimated at the end of each of experiment are also shown in the table. The relative permeabilities were affected by the oil/water emulsion formed during the coreflood experiments. It was observed that emulsions formed did not break down for up to 48 hours and sometimes beyond, after the conclusion of the experiment. The history match of pressure drop and recovery results from the simulator for all the anionic ethoxy sulphate surfactant concentrations are shown in the Appendix as Figure A6 to Figure A10.

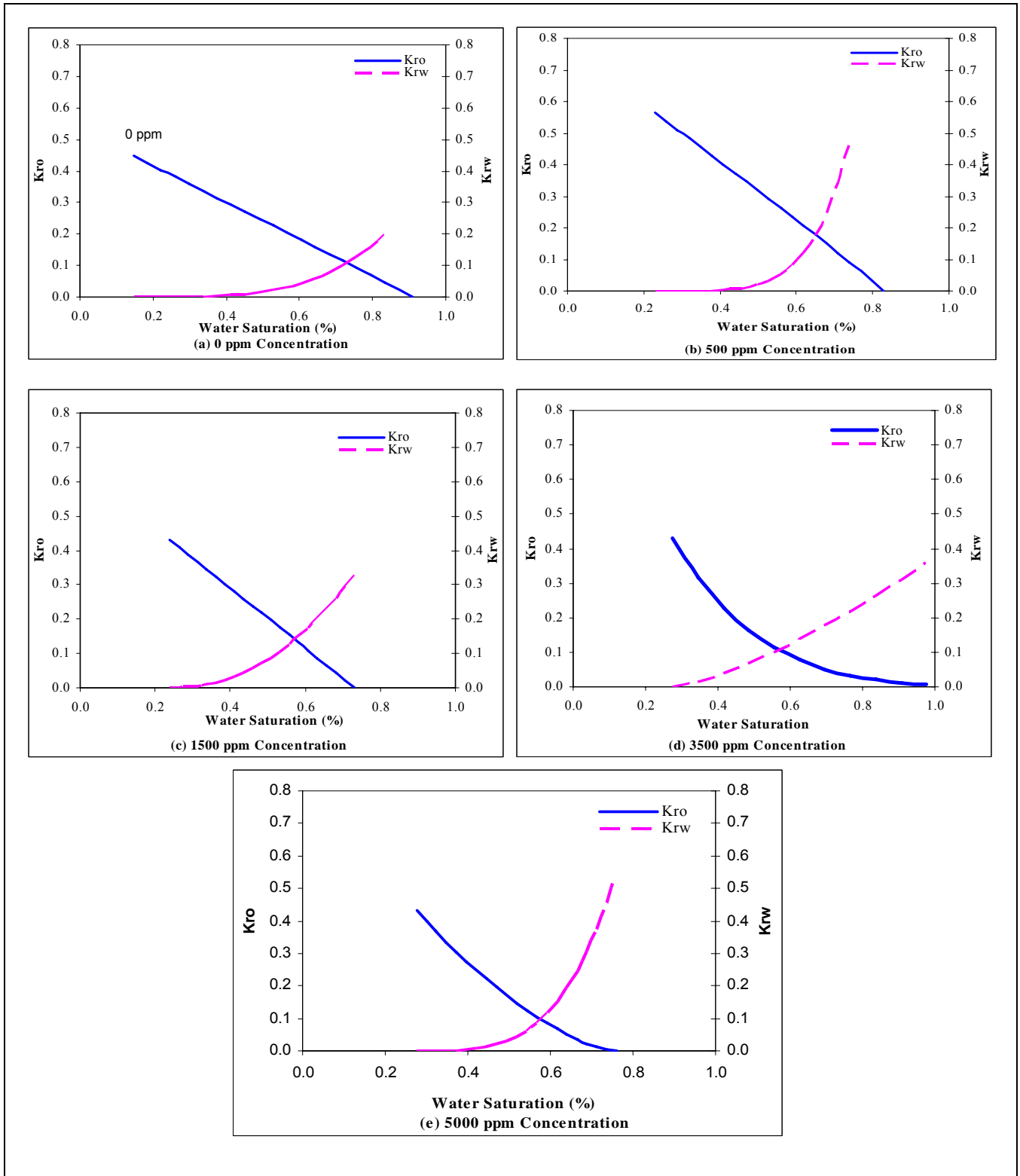


Figure 15: Relative Permeability Simulator Output of Yates Core and Live Oil at Reservoir Conditions with Anionic Ethoxy Sulphate Surfactant at Various Concentrations

The resulting relative permeability characteristics obtained from the simulator for live oil investigations at reservoir conditions and at various ethoxy sulphate surfactant concentrations are shown as Figure 15 (a-e).

For 0 ppm surfactant concentration (Figure 15 (a)), $S_{wi} = 15\% < 25\%$, $k_{rw} = 13\% < 30\%$ and $S_{w,c-o} = 71\% > 50\%$ indicate water-wet nature. However, k_{ro} of $54\% < 70\%$ and the low S_{wi} of 15 % indicate oil-wet characteristics.

Relative permeability curves at 500 ppm surfactant concentration (Figure 15 (b)) indicate water-wet characteristics ($S_{wi} = 23\% < 25\%$, $S_{w,c-o} = 65\% > 50\%$, $k_{rw} = 25\% < 30\%$). The end-point oil relative permeability of 33%, maybe attributable to formation of emulsions. .

Relative permeability curves at 1500 ppm surfactant concentration (Figure 15 (c)) indicate water wet ($S_{wi} = 24\% < 25\%$, $S_{w,c-o} = 58\% > 50\%$, $k_{rw} = 14\% < 30\%$), k_{ro} of $29\% < 70\%$ again indicates oil wet characteristics. However the value of initial water saturation S_{wi} shows that Yates core may be oil wet at this concentration.

Relative permeability curves at 3500 ppm surfactant concentration (Figure 15 (d)) indicate water wet ($S_{wi} = 28\% < 25\%$, $S_{w,c-o} = 55\% > 50\%$, $k_{rw} = 23\% < 30\%$). k_{ro} of $36\% < 70\%$ again indicates oil wet nature.

Wettability interpretations can be obtained from relative permeabilities in a similar manner even for 5000 ppm ethoxy sulphate surfactant concentration (Figure 15 (e)). Relative permeability curves at 5000 ppm surfactant concentration indicate water wet ($S_{wi} = 22\% < 25\%$, $S_{w,c-o} = 56\% > 50\%$, $k_{rw} = 13\% < 30\%$). k_{ro} of $34\% < 70\%$ again indicates oil wet nature.

Other important observations made in this investigation using the Yates live oil + ethoxy sulphate surfactant + Yates synthetic brine are summarized as follows;

1. The ethoxy sulphate surfactant showed a decrease in oil recovery in this investigation because wettability was altered from an initially weakly water wet to oil wet state. Emulsion formation was also noticed at all concentrations but more pronounced at higher concentrations during the investigation.
2. The initial water saturation was observed to increase gradually as the concentration of the anionic ethoxy sulphate surfactant was increased from 0 ppm to 5000 ppm. The initial water saturation was less than 25 % for some of the floods which indicates an oil wet characteristic of the core according to one of the Craig rules (Craig 1971).
3. The end point relative permeability to water at residual oil saturation were all less than 30 %, with the highest value observed for the 3500 ppm flood. Their values suggest water-wet tendencies, from Craig's rule.
4. A major shift to the left was observed for the crossover-point from 71% to 56% at 0 ppm and 5000 ppm surfactant concentration respectively. This crossover point shift resulted in lesser oil recovery from the Yates core
5. End-point relative permeability to oil at initial water saturation gradually decreased from 55 % to 36% in the floods as anionic surfactant concentration is increased from 0 ppm to 5000 ppm. This drop in end-point oil permeabilities may entirely be due to emulsion formation.
7. The relative permeability ratios shown in Figure 16 and fractional water flow curves shown in Figure 17 gradually shifted from right to left with increasing

concentration of anionic ethoxy alcohol surfactant. The left ward shift indicates an unfavorable alteration of Yates wettability from initially weakly water wet to oil wet.

8. As previously discussed, advancing contact angle measurements conducted in previous investigation (Xu and Rao, 2005) using anionic ethoxy sulphate surfactant in Yates stock tank oil indicated an angle of 154° – 156° which shows oil wet tendencies.

As previously mentioned, emulsion formation has profound influence on end-point relative permeabilities due to high pressure drops. Hence they cannot be alone used to infer wettability. Therefore shifts in relative permeability ratio curves (K_{rw}/K_{ro}) has been used to infer wettability alterations. The (K_{rw}/K_{ro}) plot for the live oil investigation is shown in Figure 16. The resulting fractional water flow curves computed for various surfactant concentrations are given in Figure 16.

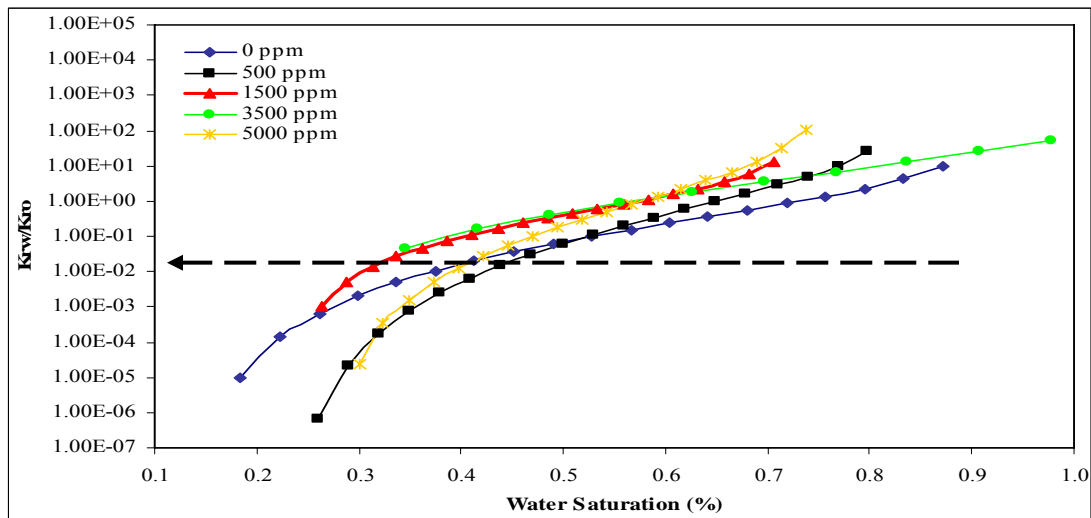


Figure 16: Coreflood Simulator Results of Relative Permeabilities Ratios at Various Anionic Ethoxy Sulphate Surfactant Concentrations for Yates Reservoir Rock Live Fluids at 82°F and 700 Psi

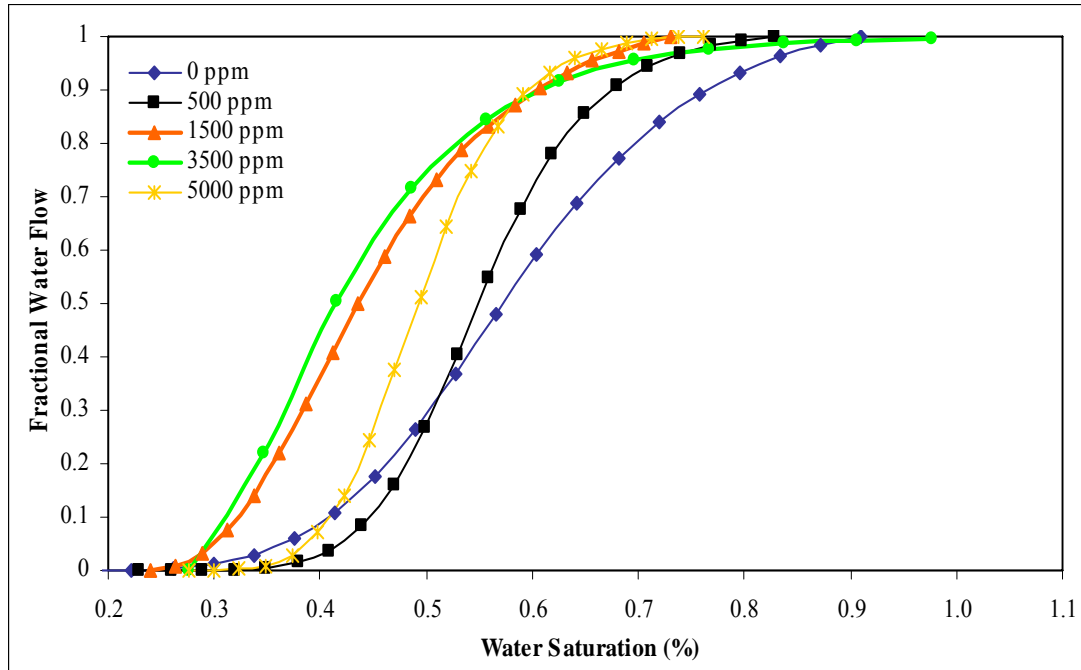


Figure 17: Effect of Anionic Ethoxy Sulphate Surfactant Concentration on Fractional Water Flow

Figure 15 show a gradual shift of relative permeability ratio curves from the right to the left as indicated by the cross over point ratio (k_{rw}/k_{ro}). This shift may be interpreted to be the development of an unfavorable wettability alteration in presence of ethoxy sulphate surfactant. The fractional water flow curve, shown in Figure 16 also shifted to the left.

4.4 Amott Wettability and Imbibition Tests

The Amott test, a well known test for the determination of the wettability of reservoir rock was used to determine the wettability of the Yates field core. It is based on the principle of spontaneous and forced imbibition of oil and water into the core. The main principle of this method is that the wetting fluids spontaneously imbibe into the core displacing the non wetting fluid. The method also requires a forced imbibition step after spontaneous imbibition. The Hassler type core holder was used to force the wetting fluid

to imbibe more into the rock pore space, and hence forcefully displace the non-wetting fluid. The difference in ratio of the volume of fluid spontaneously imbibed to the total (spontaneous and forced) fluid imbibed is used to determine the Amott wettability index. The index ranges from -1 for completely oil wet to +1 for completely water-wet formation.

The wetting phase will tend to spread on the solid surface and a porous solid will tend to imbibe the wetting phase, in both cases, displacing the non-wetting phase. Rocks can be water-wet, oil-wet or intermediate-wet. The intermediate state between water-wet and oil-wet is caused nearly equal preference of the rock to be in contact with both oil and water. This is also called “fractional wettability”.

Wettability affects relative permeability, electrical properties, nuclear magnetic resonance relaxation times and saturation profiles in the reservoir. The wetting state impacts water flooding and aquifer encroachment into a reservoir. The effect on wettability changes of different anionic surfactant concentrations were noted in section 4.4. Tables 9 and 10 and Figure 18, show the results of the wettability index measurements. The index measured for the non-ionic surfactant indicated water wetness at 0 ppm (brine) surfactant concentration and indicates a neutral wetness for higher surfactant concentrations.

Table 9: Amott Wettability Index (I_w) at Varying Concentrations of Ethoxy Alcohol Surfactant.

Surf Conc (ppm)	V_{ws} (cc)	V_{wT} (cc)	V_{osp} (cc)	V_{oT} (cc)	δ_w	δ_o	I_w
0	2.1	5.7	1.1	11.0	0.1000	0.3684	-0.2684
500	1.6	11	1.0	10.9	0.0917	0.1454	-0.0538
1500	1.4	11	1.0	10.9	0.0917	0.1273	-0.0356
3500	1.5	12	1.1	10.4	0.0956	0.1260	-0.0304
5000	1.2	15	1.4	11.8	0.1188	0.0800	0.0388

Table 10: Amott Wettability Index (I_w) at Varying Concentrations of Ethoxy Sulphate Surfactant.

Surf Conc (ppm)	V_{ws} (cc)	V_{wT} (cc)	V_{osp} (cc)	V_{oT} (cc)	δ_w	δ_o	I_w
0	2.10	5.70	1.10	11.00	0.1000	0.3684	-0.2684
500	1.35	10.45	0.45	13.35	0.0337	0.1291	-0.0954
1500	0.94	12.64	0.30	13.40	0.0224	0.0744	-0.0520
3500	0.85	11.90	0.40	14.00	0.0285	0.0714	-0.0429
5000	0.78	11.40	0.43	14.80	0.0290	0.0684	-0.0394

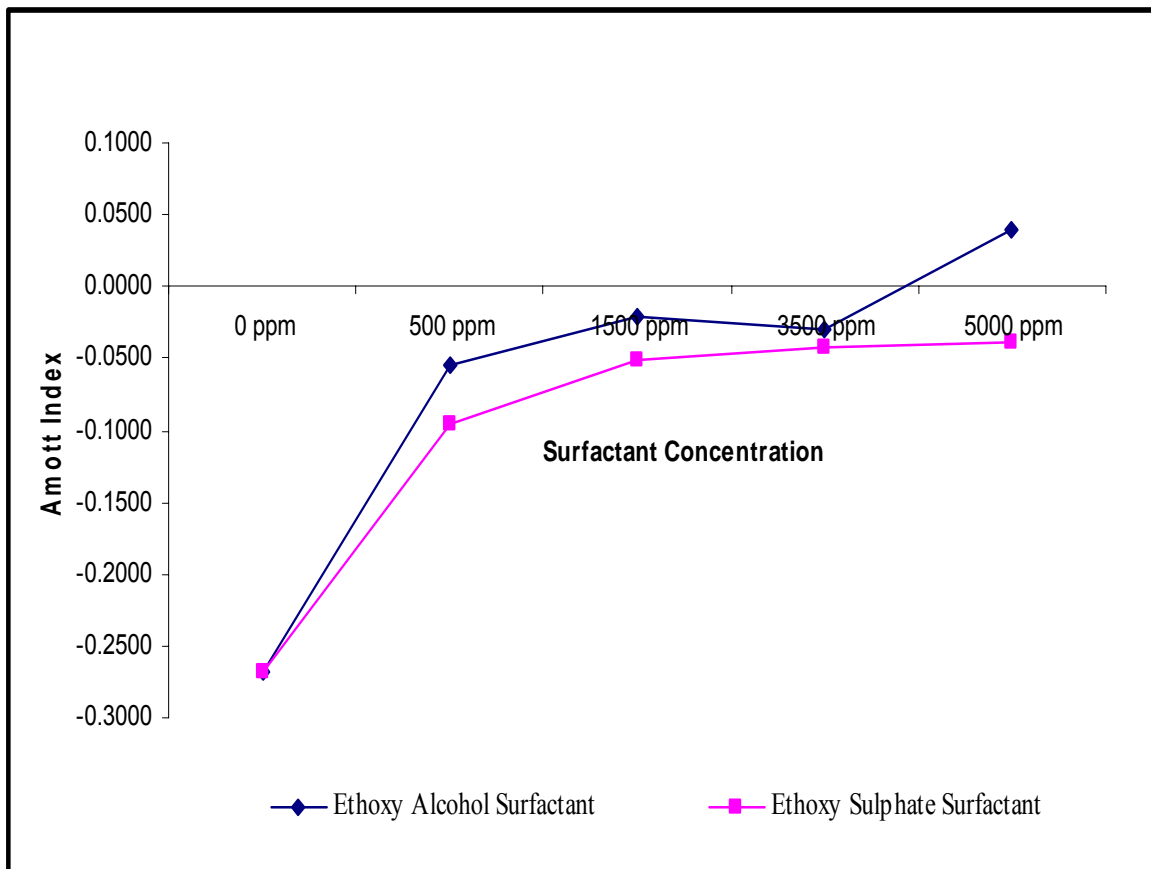


Figure 18: Amott Wettability Indices (I_w) Estimated for Various Ethoxy Alcohol Surfactant and Ethoxy Sulphate Surfactant Concentrations at Ambient Conditions.

4.5 Summary of Results and Further Analysis

Table 11: Summary of Results of Contact Angle and Capillary Number for Yates Field Cores Using Yates Brine, Nonionic Ethoxy Alcohol and Anionic Ethoxy Sulphate Surfactants for Yates Live and Stocktank Oil at Reservoir Conditions (Rao et al, 2004)

Rock-Fluids System	Test Conditions P (Psi) / T (°F)	Surfactant Type	Surfactant Conc. (ppm)	Contact Angle/		Coreflood Recovery (% OOIP)	Cosine of contact angles (θ)	$\sigma(\text{Cos } \theta)$	$I/\sigma \text{Cos } \theta$	$N_{ca} = \frac{v\mu}{\sigma \text{Cos } \theta}$	$N_{ca} = \frac{v\mu}{\sigma}$
				$\theta_a (^\circ)$	IFT (N/m)						
Dolomite-Yates stocktank oil-Yates brine	700 / 82	Nonionic Ethoxy Alcohol	0	155	0.0322	67.47	-0.9063	-0.0292	-34.27	-6.94E-07	6.293E-07
			500	154	-	71.90	-0.8987	-	-	-	-
			1000	154	0.0047	-	-0.8987	-0.0042	-236.75	-4.80E-06	4.311E-06
			1500	-	-	72.24	-	-	-	-	-
			3500	154	0.0029	73.26	-0.8987	-0.0026	-386.36	-7.83E-06	7.036E-06
			5000	-	-	65.17	-	-	-	-	-
Dolomite-Yates stocktank oil-Yates brine	700 / 82	Anionic Ethoxy Sulphate	0	155	0.0327	67.38	-0.9063	-0.0296	-33.76	-6.84E-07	6.201E-07
			500	139	0.0002	64.82	-0.7547	-0.0002	-6022.86	-1.22E-04	9.211E-05
			1500	-	-	72.43	-	-	-	-	-
			3500	-	0.0001	71.99	-	-	-	-	2.53E-04
			5000	-	-	63.20	-	-	-	-	-
Dolomite-Yates live oil-Yates brine	700 / 82	Nonionic Ethoxy Alcohol	0	55	0.0235	66.00	0.5735	0.0135	74.20	1.50E-06	8.623E-07
			500	65	0.0067	70.00	0.4226	0.0028	353.18	7.16E-06	3.024E-06
			1500	85	0.0044	86.00	0.0872	0.0004	2600.43	5.27E-05	4.595E-06
			3500	82	0.0018	81.00	0.1392	0.0002	4013.36	8.13E-05	1.132E-05
			5000	-	-	71.00	-	-	-	-	-
Dolomite-Yates live oil-Yates brine	700 / 82	Anionic Ethoxy Sulphate	0	55	0.0235	75.60	0.5736	0.0135	74.19	1.50E-06	8.623E-07
			500	140	0.0025	65.40	-0.7660	-0.0019	-528.54	-1.07E-05	8.204E-06
			1500	120	0.0016	57.00	-0.5000	-0.0008	-1257.86	-2.55E-05	1.274E-05
			3500	135	0.0010	47.00	-0.7070	-0.0007	-1458.17	-2.95E-05	2.089E-05
			5000	-	-	46.50	-	-	-	-	-

Table 11 shows oil recoveries obtained from the corefloods, the contact angles and IFT's measured from previous investigations at reservoir conditions (Xu, 2004) and capillary numbers estimated for various concentrations of nonionic and anionic surfactant. The results from the Table 11 are plotted in Figures 19 and 20 for better comparison. The Figures 19 and 20 show the plots of oil recoveries obtained for live oil corefloods using both nonionic ethoxy alcohol and anionic ethoxy sulphate surfactants against capillary numbers, $N_{ca}^* = \frac{V\mu}{\sigma \cos \theta}$ and $N_{ca} = \frac{v\mu}{\sigma}$, respectively. The brine viscosity of 9.24E-04 kg/m.s and the flood velocity of 2.19E-05 m/s were used in

capillary number calculations. Figure 19 shows an increase in oil recovery with increasing capillary numbers for live oil corefloods with both the surfactants. This is in conformance with the typical capillary number relationship with residual oil saturation. The equation used for capillary number estimation in Figure 19 considered the contact angle term in the formulation ($N_{ca}^* = V\mu/\sigma\cos\theta$) for live oil at reservoir conditions. However, the trend of increasing oil recovery with increasing capillary number was observed only for nonionic surfactant, while the effect was reversed in the case of the anionic surfactant in Figure 20. The capillary number in Figure 20 was computed by ignoring the contact angle by setting contact angle equal to 0° in the formulation ($N_{ca} = V\mu/\sigma$). This plot (Figure 20) indicates that ignoring contact angles in capillary number formulations is an erroneous assumption. Thus, the comparison of Figures 19 and 20 clearly demonstrate the importance of contact angles in the estimation of capillary number and in establishing oil recovery versus capillary number relationships.

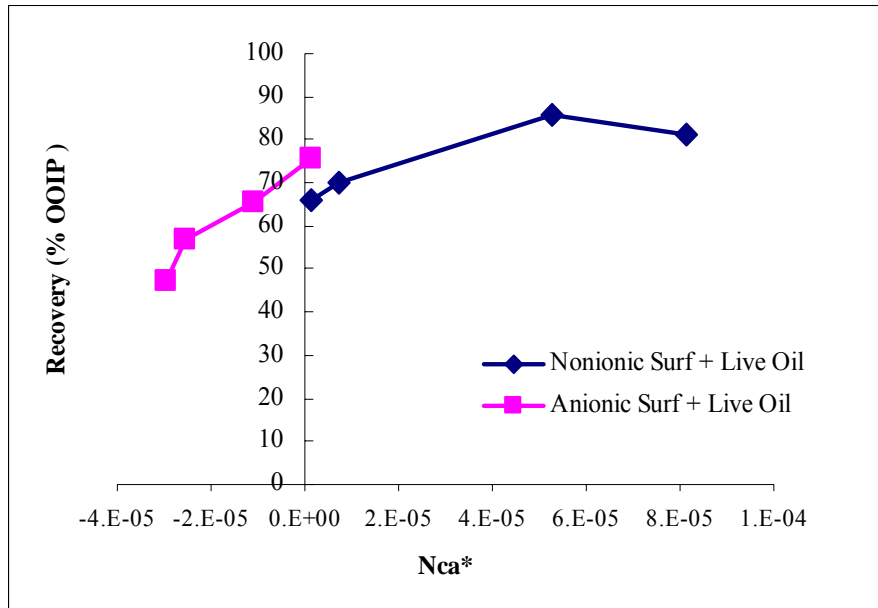


Figure 19: Oil Recoveries versus Capillary Number ($V\mu/\sigma\cos\theta$) for Live Oil in Yates Rock-Fluid system

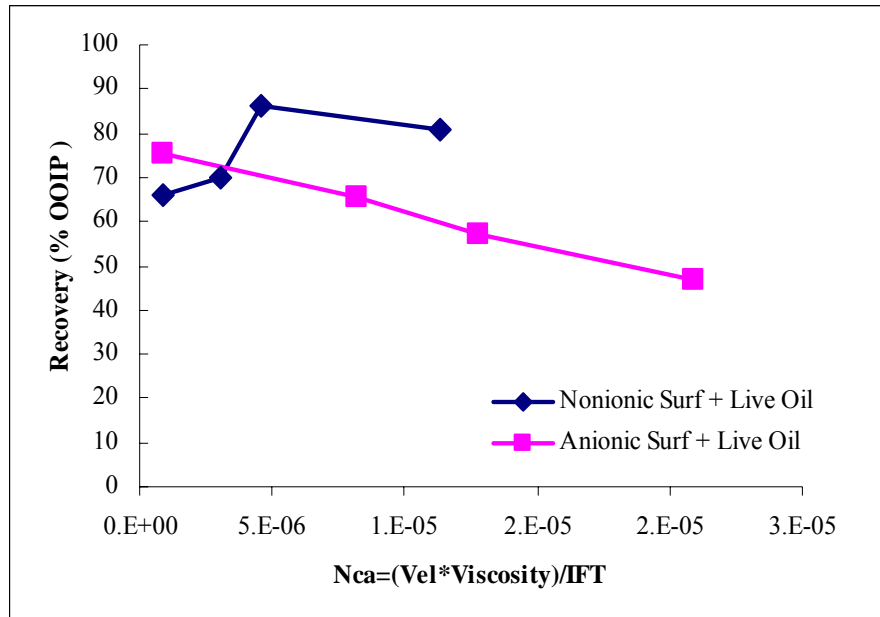


Figure 20: Oil Recoveries versus Capillary Number ($V\mu/\sigma$) for Live Oil in Yates Rock-Fluid System

4.6 Mechanism for Wettability Alteration

The reactive system of Yates rock + Yates synthetic brine + Yates crude oil has been previously shown to be oil wet from coreflood data conducted at ambient conditions (Ayirala, 2002). The Amott wettability index as shown in Tables 9 and 10 has further shown this to be true. Figure 18 show a cluster around intermediate wettability state at surfactant concentration of 500 ppm and above for both nonionic ethoxy alcohol and anionic ethoxy sulphate surfactant. The addition of surfactant to the system at various concentrations by coreflooding gradually shifted the wettability to a mixed wettability state Ayirala and Rao (2004), which therefore improved oil recovery. This mixed wettability was not observed in the ethoxy sulphate surfactant. Two important mechanisms necessary for mixed wettability development are the thin water film stability (Lin et al., 2002) and orientation of surfactants molecules (Spinler 1996). When the thin wetting water film is stable, oil exists as globules in the middle of bigger pores and water

spreads between the oil and the rock surface. The thin liquid film becomes unstable in the presence of surfactant molecules due to the adsorption of the molecules on the rock surface. The instability of the thin water film at the interface creates a continuous oil-wet path for displacement of oil. This is responsible for the mixed wettability situation observed (Ayirala, 2002).

Rao and Ayirala (2004) also proposed a sequential diffusion and adsorption of surfactant molecules into the medium through natural fractures. The surfactant diffuses into the rock, interacts with the rock surface, alters physico-chemical properties of the rock surface and thus creates a continuous path for the production of oil on the rock surface. This process is repeated as additional surfactant is being injected into the producing formation.

Spinler, (1996) used the orientation of surfactant molecule to explain the phenomenon. Surfactants possess amphipolar and amphatic characteristics. They have a hydrophilic head and hydrophobic tail. These characteristics of surfactant are responsible for its affinity for interface between immiscible liquids. A surfactant molecule can orient itself on a solid surface in different ways. The position of the head or tail of the surfactant to a large extent determines the wettability of the rock surface.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Summary of Investigations, Findings and Conclusions

Reservoir condition investigation was conducted using Yates field rock and fluids in this study to determine wettability alteration capability of surfactants for enhancement of oil recovery in Yates field. Coreflood experiments were conducted at various concentrations of nonionic (ethoxy alcohol) and anionic (ethoxy sulphate) surfactants. Oil/water relative permeabilities were estimated using a coreflood simulator to history match the recovery and pressure drop data obtained from the displacements. The relative permeability variations were interpreted using the Craig's rule of thumb to characterize the wettability alterations induced by the surfactants. Imbibition tests were also conducted at ambient conditions to infer the wettability shifts caused by these surfactants by measuring the Amott wettability indices using Yates field core, Yates stocktank oil and Yates synthetic brine .

The findings from the investigations are as follows:

1. The nonionic ethoxy alcohol surfactant was effective in enhancing oil recovery in Yates field core containing Yates live oil as the oleic phase and Yates synthetic brine as the aqueous phase at Yates reservoir conditions. Nonionic ethoxy alcohol surfactant resulted in an increase in oil recovery at reservoir conditions from 66% at 0 ppm surfactant concentration to 86% at 1500ppm surfactant concentration. This is due to the ability of this surfactant to develop mixed-wettability in Yates rock-fluids system. The high oil recoveries as well as the gradual shifts to the right in k_{rw}/k_{ro} curves confirm the mixed wettability development due to the

presence of nonionic surfactant. Previous investigation conducted by Ayirala and Rao (2004) using Yates stock tank oil and Berea sandstones at ambient conditions also reported the unique capability of the nonionic ethoxy alcohol surfactant to develop mixed-wettability in reservoir rock-fluid systems. However, the advancing contact angles reported by Xu (2005) with nonionic surfactant in the same Yates rock-live oil-brine system at reservoir conditions indicated wettability alterations from initially weakly water wet (55° at 0 ppm) to intermediate-wet (85° at 1500 ppm) by the surfactant. This disagreement between corefloods and contact angles can be attributed to the heterogeneity of mixed-wettability, wherein only the gradual rightward shifts in relative permeability ratio curves apart from very high oil recoveries in an initially water-wet system have been identified so far as the unique means to quantify mixed- wettability.

2. The anionic ethoxy sulphate surfactant altered the wettability of Yates rock-live oil-brine system from and initially weakly water-wet to strongly oil-wet. The gradual decrease in oil recoveries (from 76% at 0 ppm to 47% at 5000 ppm surfactant concentration) as well as the relative shifts to the left in k_{rw}/k_{ro} curves corroborate the wettability alterations to strongly oil-wet, induced by the surfactant. The advancing contact angle measured in the same rock-fluids system at reservoir conditions (Xu, 2005) also support this wettability alterations inferred from the corefloods (water advancing contact angles changing from 55° at 0 ppm to 165° at 1000 ppm).
3. In Yates stocktank oil-brine-Yates dolomite system at Yates reservoir conditions, the nonionic surfactant has resulted in increased oil recoveries from 67% at 0 ppm

- to 73% at 3500 ppm (Rao et al, 2005). The small increments in oil recoveries as well as the gradual shifts to the right in k_{rw}/k_{ro} curves indicate the wettability alterations from an initially strongly oil-wet to a less oil-wet state. However, the advancing contact angles measured by Xu (2005) in the same rock-fluids system at reservoir conditions indicated insignificant wettability alterations from the initial strongly oil-wet state (154° at 0 ppm to 152° at 3500 ppm). This suggests that the incremental oil recovery of about 6 % over 0 ppm flood appears to be due to reduction in oil-water IFT.
4. The anionic surfactant has resulted in increments in oil recoveries from 67% at 0 ppm to 72% at 1500 ppm in Yates stocktank oil containing rock-fluids system at Yates reservoir conditions (Rao et al, 2005). These small increments in oil recoveries and the gradual shift to the right in the relative permeability ratio (k_{rw}/k_{ro}) curves indicate the wettability alterations from an initial oil-wet to less oil-wet state also due to this surfactant. The advancing contact angles reported by Xu (2005) also confirm the wettability shifts inferred from coreflood relative permeabilities (154° at 0 ppm to 120° at 1500 ppm).
 5. The Amott wettability index (-0.2684) measured showed oil-wet tendency for Yates stocktank oil-brine-Yates dolomite system at ambient conditions. This initial wettability is gradually altered to less oil-wet or intermediate-wet by both the surfactants used in this study (from -0.2684 at 0 ppm to -0.0304 at 3500 ppm for nonionic surfactant and from -0.2684 at 0 ppm to -0.0429 at 3500 ppm for anionic surfactant). Ayirala et al. (2004) have reported similar wettability shifts by conducting contact angle measurements using Yates stocktank oil, brine and

dolomite rock substrates at ambient conditions with both the surfactants (156° at 0 ppm to $115\text{-}125^\circ$ at 500 ppm).

6. The result was further analyzed using capillary number, the recover versus capillary number shows that ignoring contact angles in capillary number formulations is an erroneous assumption, as oil recovery was observed to increase with increasing capillary number for the capillary number formation which honored the contact angle and the trend was reversed when the contact angle was ignored.

Thus this study has demonstrated, through corefloods, imbibition tests and comparison with reported contact angle measurements, different wettability altering characteristics of surfactants such as oil-wet to less oil-wet, water-wet to mixed-wet, weakly water-wet to intermediate-wet and weakly water-wet to oil-wet. It is also interesting to note that in almost all cases corefloods and imbibition tests corroborated well with contact angle measurements, except for Yates live oil with nonionic surfactant case where corefloods indicated mixed wettability, while contact angles indicated intermediate wettability. The following important concluding remarks can be made on the use of surfactants for improved oil recovery applications in the field with the knowledge gained from this study.

The surfactant-induced wettability alteration process is beneficial for field implementation in oil-wet fractured reservoirs. In oil-wet fractured reservoirs, the effective matrix-fracture mass transfer can be achieved by surfactant-induced wettability alterations to either less oil-wet or water-wet. The surfactant in the fracture first diffuses into the matrix and alters the wettability, enabling imbibition of even more surfactant into

the matrix. This sequential diffusion-imbibition process can result in improved oil recovery. The optimum surfactant concentration versus the enhanced oil recovery governs the economics of this process in the field.

In initially water-wet or weakly water-wet fractured reservoirs, the surfactant-induced wettability alteration process is beneficial only if the surfactant induces mixed wettability or intermediate wettability. This process is detrimental for improved oil recovery if the surfactant induces the oil-wet behavior. Thus, the surfactant type (ability to result in favorable wettability alteration), rock mineralogy and the surfactant concentration are critical in determining the economic success of this process in the field.

5.2 Recommendations for Future Work

In this current investigation, Amott wettability tests were conducted at ambient conditions, which showed a different wettability from that indicated by live oil corefloods at reservoir conditions. This discrepancy may be due to the differences in composition of the stocktank oil compared to that of live oil. Imbibition tests should also be conducted at reservoir conditions, as this will shed more light on surfactant implications and wettability alteration.

Also, the wide window of wettability interpretation from Amott index of -1 for completely oil-wet to +1 for completely water-wet can be narrowed by using both the USBM imbibition and Amott-Harvey tests for results comparison and analysis.

The average and frontal water saturations could not be measured using the current coreflooding apparatus. Future investigation could perhaps include computer tomography images to show the saturations in the core with flooding using different surfactant concentrations. Findings from the scan will help to further explain the reason behind

optimum surfactant concentration observed in some of the floods. An economic analysis, will help to clarify the successful implementation of this project on a field scale.

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APPENDIX: HISTORY MATCH OF PRESSURE DROP AND OIL RECOVERY AND RESULTING RELATIVE PERMEABILITIES FROM SIMULATOR

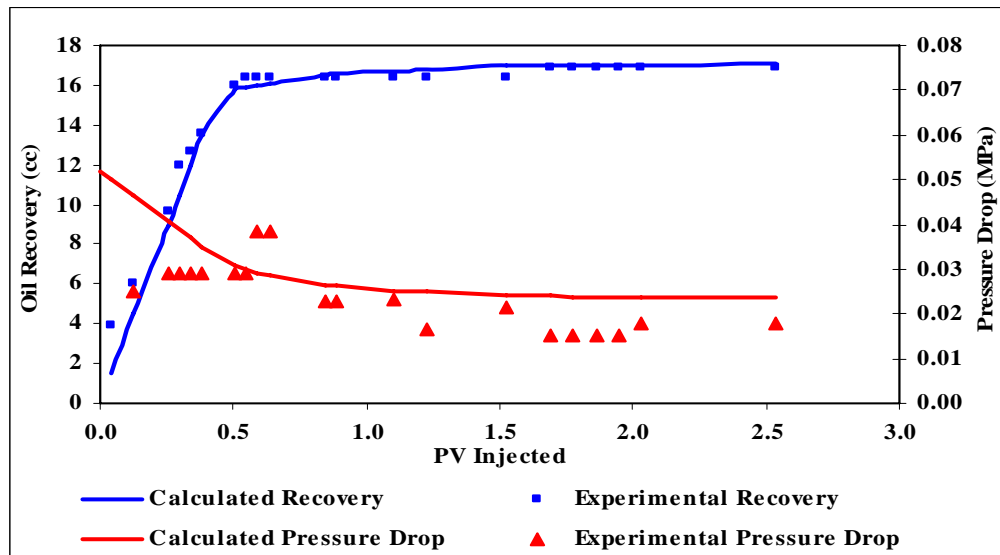


Figure A1: Coreflood Simulator Output for Brineflood of Yates Live Oil with Nonionic Surfactant Concentration of 0 ppm

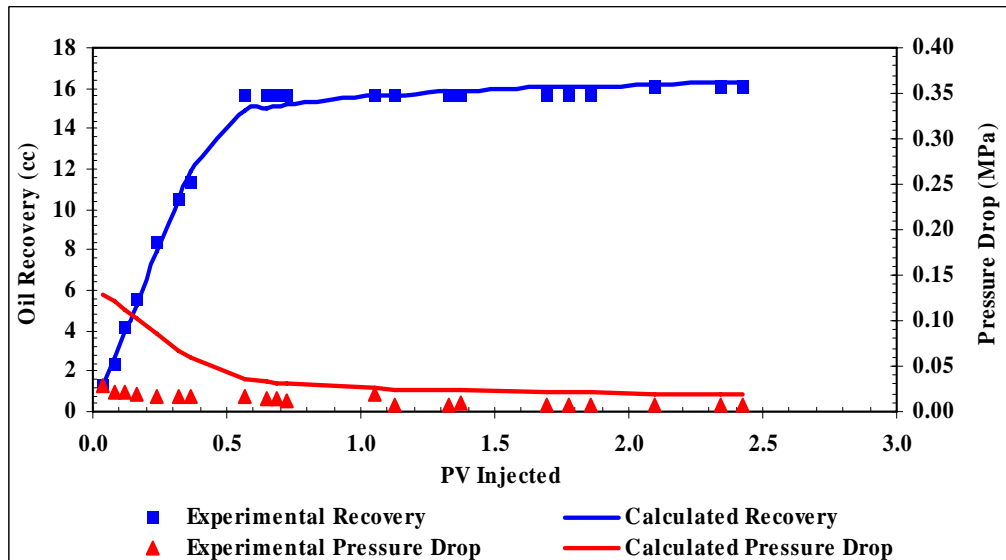


Figure A2: Coreflood Simulator Output for Brineflood of Yates Live Oil with Nonionic Surfactant Concentration of 500 ppm

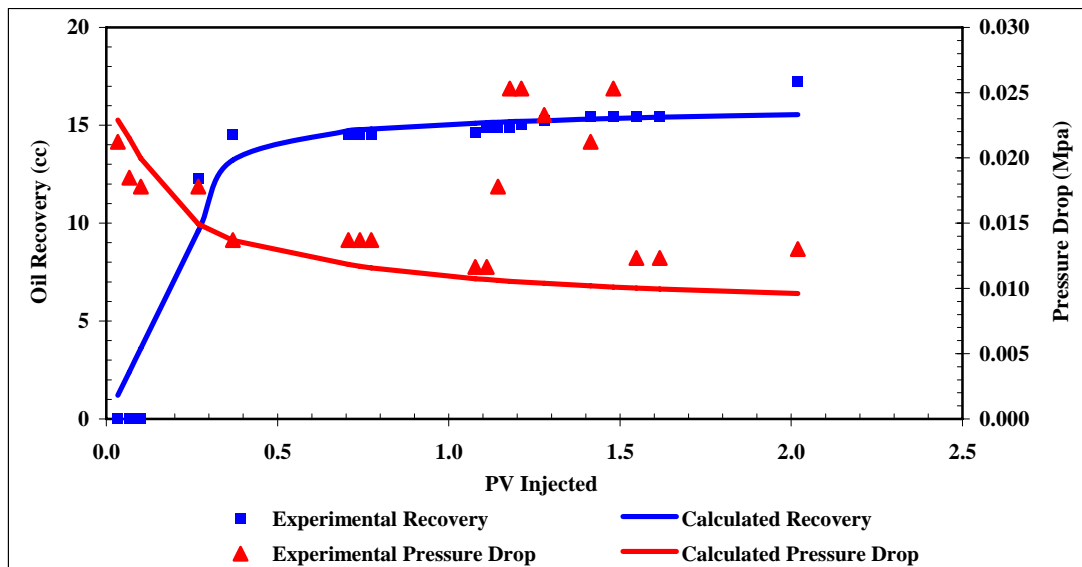


Figure A3: Coreflood Simulator Output for Brineflood of Yates Live Oil with Nonionic Surfactant Concentration of 1500 ppm

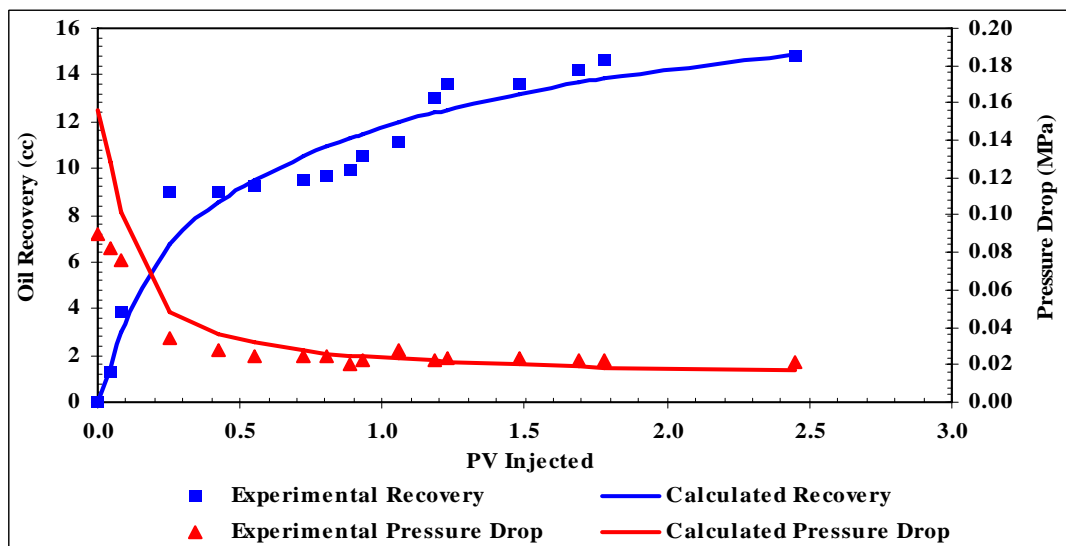


Figure A4: Coreflood Simulator Output for Brineflood of Yates Live Oil with Nonionic Surfactant Concentration of 3500 ppm

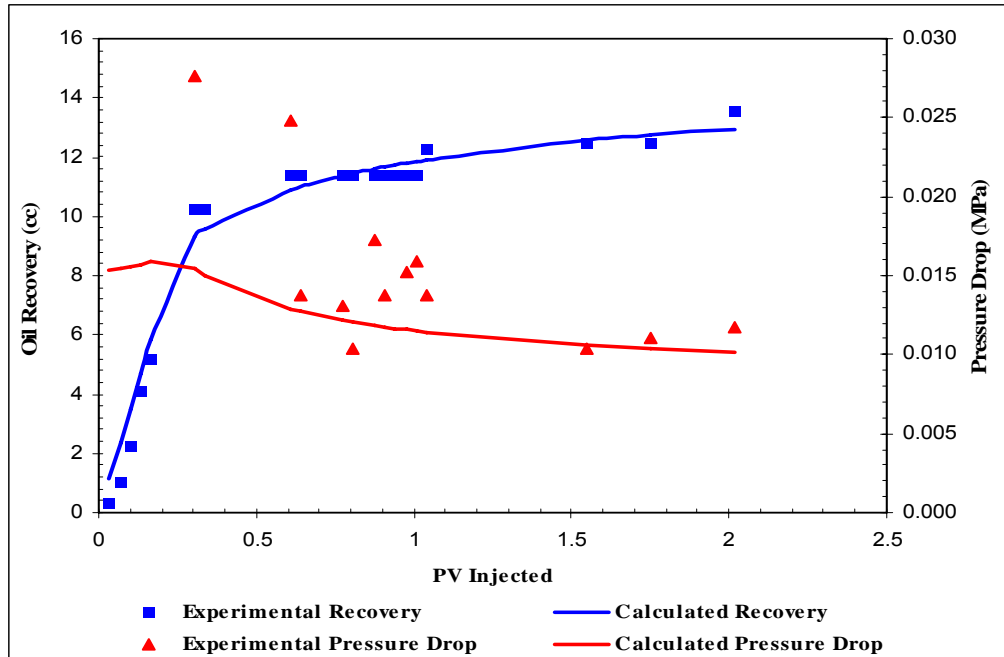


Figure A5: Coreflood Simulator Output for Brineflood of Yates Live Oil with Nonionic Surfactant Concentration of 5000 ppm

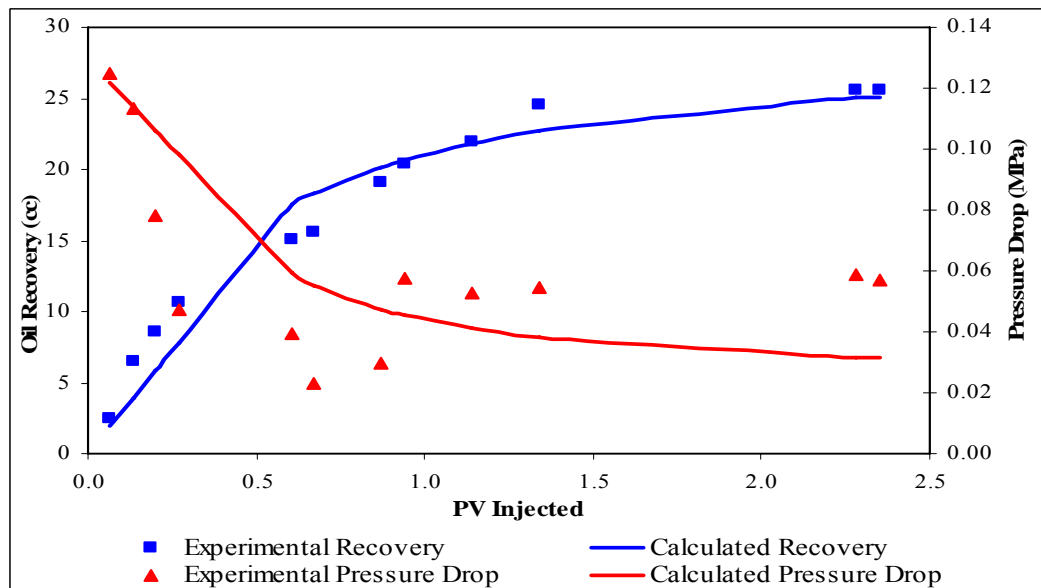


Figure A6: Coreflood Simulator Output for Brineflood of Yates Live Oil with Anionic Surfactant Concentration of 0 ppm

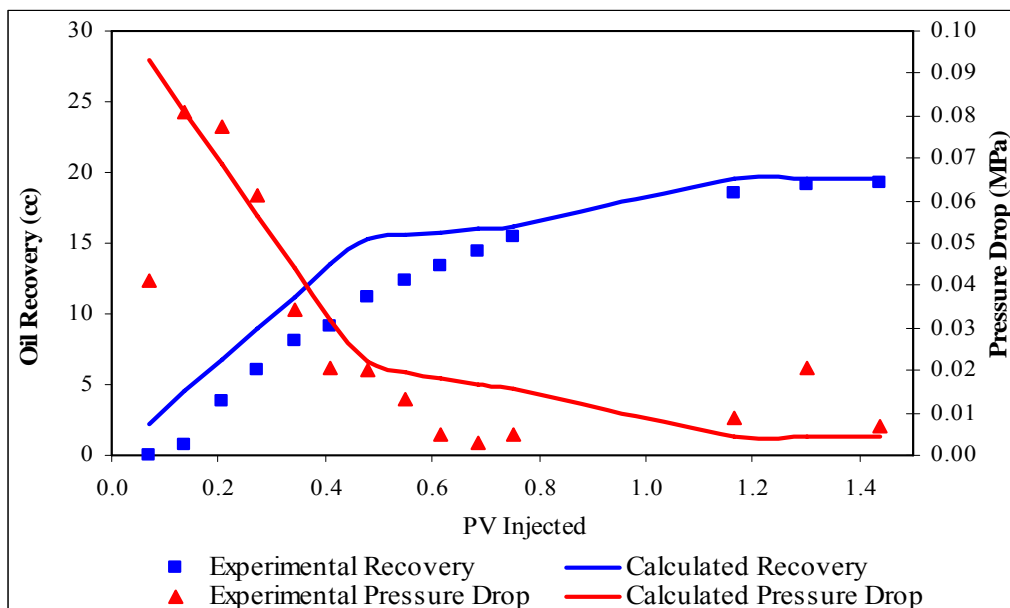


Figure A7: Coreflood Simulator Output for Brineflood of Yates Live Oil with Anionic Surfactant Concentration of 500 ppm

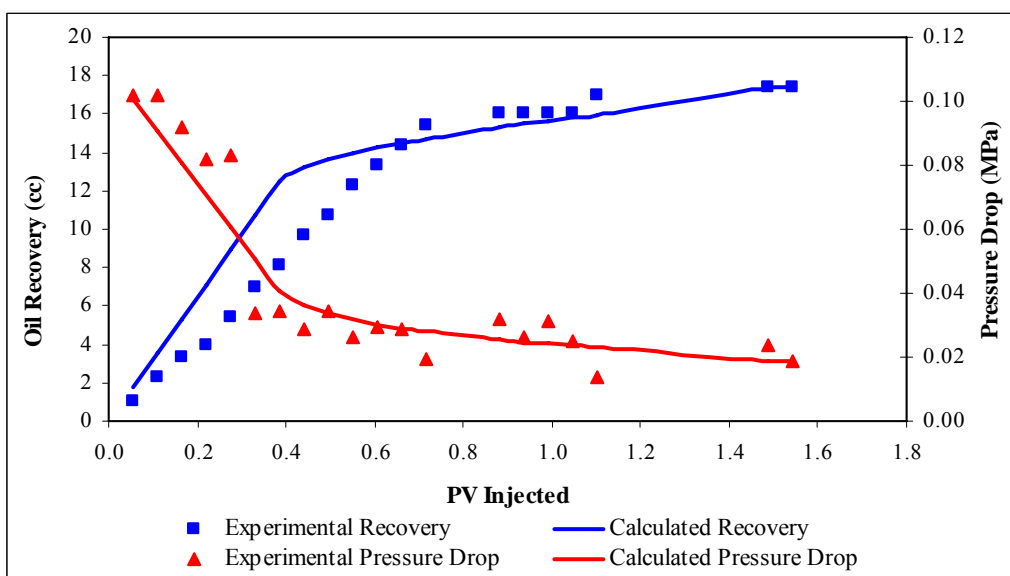


Figure A8: Coreflood Simulator Output for Brineflood of Yates Live Oil with Anionic Surfactant Concentration of 1500 ppm

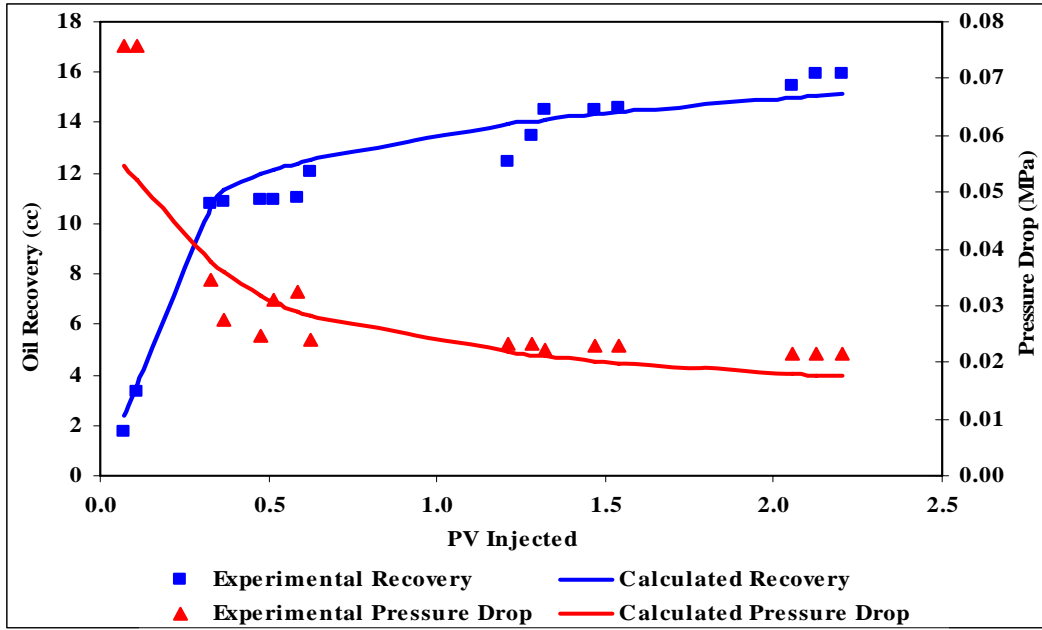


Figure A9: Coreflood Simulator Output for Brineflood of Yates Live Oil with Anionic Surfactant Concentration of 3500 ppm

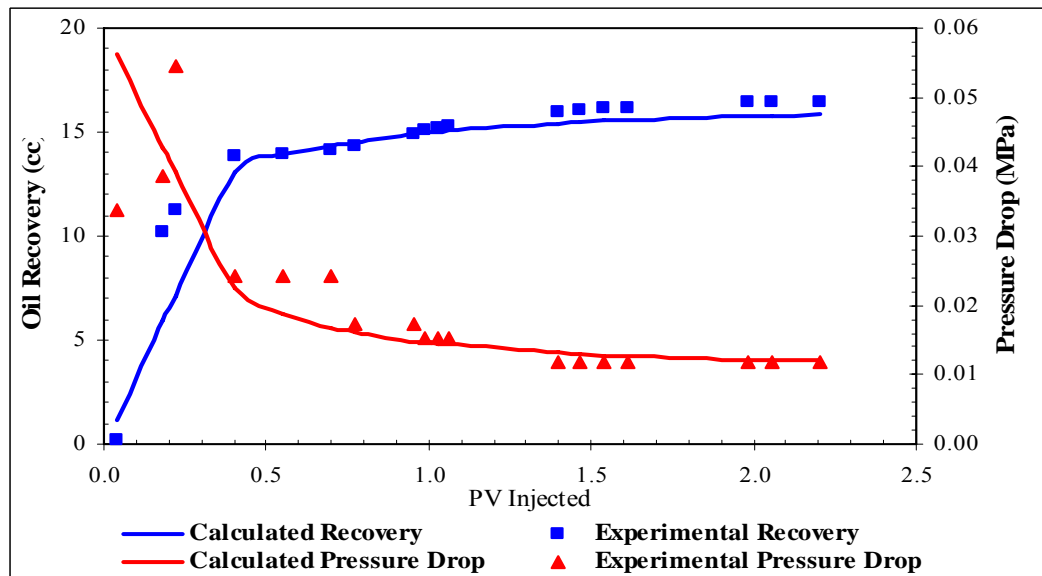


Figure A10: Coreflood Simulator Output for Brineflood of Yates Live Oil with Anionic Surfactant Concentration of 5000 ppm

VITA

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